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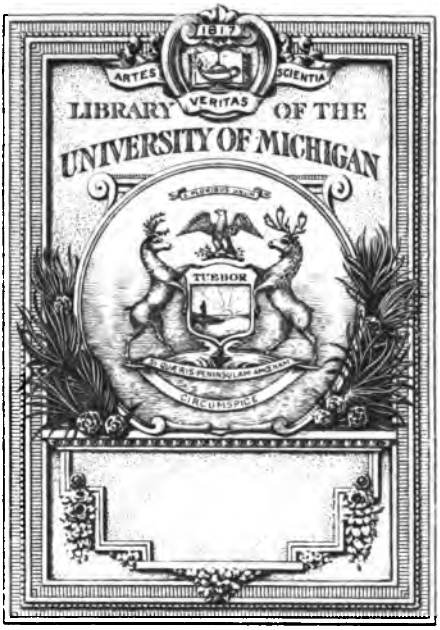

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THE MANUFACTURE OF INTERMEDIATE PRODUCTS FOR DYES

THE MANUFACTURE OF INTERMEDIATE PRODUCTS FOR DYES

MACMILLAN AND CO., Limited
LONDON . BOMBAY . CALCUTTA . MADRAS
MELBOURNE

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DALLAS . SAN FRANCISCO

THE MACMILLAN CO. OF CANADA, Ltd.
TORONTO

THE MANUFACTURE OF INTERMEDIATE PRODUCTS FOR DYES

BY

JOHN CANNELL CAIN

D.Sc. (Manchester); F.I.C.

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SECOND EDITION

WITH 25 ILLUSTRATIONS

MACMILLAN AND CO., LIMITED
ST. MARTIN'S STREET, LONDON
1919

First Edition, 1918
Second Edition, 1919

PREFACE

NOTHING is more important in the present revival of the aniline dye industry in England and America than a knowledge of the literature dealing with the manufacture of intermediate products. The scope of most of the books on the subject to which one naturally turns is necessarily limited, and the authors must perforce content themselves with describing the chemistry of the processes concerned. It is, however, of prime importance to the would-be manufacturer to have, in a convenient form, detailed information as to the preparation of the materials he proposes to make, so that he may be sure that he will not spend time and money in rediscovering, perhaps, some process that may have been already elaborately described in an obscure book or periodical.

The chemist, confronted with the task of compiling such information, immediately encounters difficulties. It is rarely that he has ready access to a good technical library, and even if that difficulty is overcome, and much time and labour are spent in the search, he will be chary of asserting that he has exhausted the whole of the literature on the subject of his investigation.

It appeared to the author that a concise account of the literature dealing with the manufacture of intermediate products for dyes might therefore be of considerable use, and in this book he has endeavoured to present such an account in detail so as to render it unnecessary to refer to the original descriptions.

It may perhaps be stated that he doubts whether any single library in England contains the whole of the literature consulted.

As a guide to the selection of these materials the author has made considerable use of the "Dyestuff Census of the United States" (published in the *Journal of the Society of Chemical Industry*, 1916, **35**, 1202), as well as of other information as to the dyes in general use, and believes that he has included all the more important intermediate products.

The aim has been to record the most recent or the most trustworthy method of manufacture of each substance in the same detail as in the original publication, to mention other processes or modifications, and to record essential scientific data, such as melting points, boiling points, densities, solubilities, etc. The pure chemistry of the subject has been left alone as it is readily available.

It has not been possible to attain this aim in all cases, for although the manufacture of certain products has been previously described in the most minute detail (see, for example, the description of the manufacture of diethyl-*m*-aminophenol, p. 121), the only references to others are accounts of laboratory experiments.

Both, however, have their uses: improvement of elaborately described processes can often be made (in the above instance conspicuously so); in any event it will be rare that such a process will be blindly imitated, and the description of a laboratory experiment can often be rapidly developed to a large scale manufacture.

In a few cases the author has supplemented published descriptions by his own experience, and in certain important instances (for example, phenylglycine and anthrarufin) practically all the published processes are given in full.

Throughout the book the original weights and volumes, method of indicating density, etc., are reproduced. The latter can easily be converted, if required, by means of the tables in the Appendix.

Details of certain frequently occurring operations, such as sulphonation, etc., are not, of course, repeated. Thus chlorination is treated very fully under Chlorobenzene and Benzyl chloride, nitration under Nitrobenzene, reduction under Aniline, sulphonation under Phenol, and so on.

It seemed superfluous to reproduce figures of ordinary plant such as sulphonation pans, filter presses, etc., which are illustrated in the advertisement columns of periodicals such as the *Journal of the Society of Chemical Industry* and the *Journal of Industrial and Engineering Chemistry*, and the author has therefore contented himself with giving diagrams of special plant, which are, perhaps, not quite so readily available. In this connexion his grateful thanks and acknowledgments are due to Dr. R. Seligman, of the Aluminium Plant and Vessel Co., for the loan of the block of Fig. 15, to M. P. Blondel for permission to reproduce Figs. 4, 6, 7, 8, 11, and 23 from *La Revue des Produits* *chimiques*, and to Messrs. Davis Bros. for similar kindness with regard to Figs. 5, 13 and 14, which were first published in *The Chemical Trade Journal*.

In conclusion, the hope may be expressed that the book may be found useful, not only to manufacturers and technical chemists, but also to students of chemistry in technical schools and universities.

LONDON, *February*, 1918.

PREFACE TO SECOND EDITION

IN the short period since this book was first published, considerable additions have been made to the scientific and technical literature of the subject, particularly in America. These have been duly incorporated in the present revision of the book; several of the descriptions have also been expanded, and some useful suggestions made by the reviewers have been adopted.

LONDON, *March*, 1919.

CONTENTS

CONTRACTIONS EMPLOYED IN THIS VOLUME

D^{15}_{15}	Density at 15° compared with water at 15°.
b.p.	Boiling point.
m.p.	Melting point.
(Temperature is in degrees Centigrade).	
E.P.	English Patent.
F.P.	French Patent.
G.P.	German Patent.
G. P. Anm	German Patent Anmeldung (Application).
U.S.P.	United States Patent.

ABBREVIATED TITLE.	JOURNAL.
Amer. Chem. J.	American Chemical Journal.
Annalen	Annalen der Chemie.
Atti R. Accad. Sci. Torino.	Atti della Reale Accademia delle Scienze di Torino.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Bull. Soc. chim.	Bulletin de la Société chimique de Paris.
Bull. Soc. Mulhouse	Bulletin de la Société industrielle de Mulhouse.
Chem. and Met. Eng.	Chemical and Metallurgical Engineering.
Chem. Ind.	Die chemische Industrie.
Chem. Trade J.	The Chemical Trade Journal.
Chem. Zeit.	Chemiker Zeitung.
Chem. Zeitsch.	Chemische Zeitschrift.
Cotton.	Cotton (Atlanta, Ga.).
Dingl. Polyt. J.	Dingler's Polytechnisches Journal.
Gazzetta	Gazzetta Chimica Italiana.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. pr. Chem.	Journal für praktische Chemie.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers	Journal of the Society of Dyers and Colourists.
Met. and Chem. Eng.	Metallurgical and Chemical Engineering.*
Mon. Sci.	Moniteur Scientifique.
Phil. Mag.	Philosophical Magazine.
Proc..	Proceedings of the Chemical Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Rec. trav. chim.	Recueil des Travaux chimiques des Pays-Bas et de la Belgique.
Rev. prod. chim.	La Revue des Produits chimiques.
Trans.	Transactions of the Chemical Society.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. Chem.	Zeitschrift für Chemie.
Zeitsch. Chem. Ind.	Zeitschrift für die chemische Industrie.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Farb. Ind.	Zeitschrift für Farben-Industrie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, etc.

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* Title changed to "Chemical and Metallurgical Engineering," July, 1918.

THE MANUFACTURE OF INTERMEDIATE PRODUCTS FOR DYES

INTRODUCTION

The manufacture of intermediate products for dyes dates from the discovery of mauveine by Perkin in 1856 and the consequent necessity of the production of nitrobenzene, and from it aniline, on the large scale. The " aniline " of that period, owing to the imperfect methods of separating benzene and toluene, naturally contained toluidine, and the crude mixture was, curiously enough, admirably adapted for making magenta. A few years later (1863), dinitrobenzene was manufactured and reduced to *m*-phenylenediamine for the purpose of making Manchester brown, followed by dimethylaniline, diphenylamine, benzyl chloride, and other derivatives of benzene and toluene.

About the year 1869 came the demand for anthraquinone and hence for a purer form of anthracene than had up to that time been produced.

During this period naphthalene also had not been neglected, for Perkin manufactured aminoazonaphthalene (from α-naphthylamine) and Martius discovered, in 1864, dinitronaphthol (Manchester yellow).

As a consequence of Baeyer's discovery of the phthaleins in 1871 a demand for phthalic anhydride and resorcinol made itself felt for the production of the eosines in 1874.

In the following year, sulphonated derivatives of aniline, naphthylamine, and the naphthols were required for the production of soluble azo-dyes, and from this period the manufacture of naphthalene derivatives was seriously prosecuted. Its full development, however, followed the introduction of the azo-dyes derived from diamines such as benzidine, tolidine, dianisidine, etc., which dye cotton directly without a mordant, and particularly certain aminonaphtholsulphonic acids (γ-acid, H-acid, J-acid, S-acid, etc.) have been of enormous value to the industry. Progress in the manufacture of all branches of intermediate products has developed gradually and no particularly outstanding new discovery has to be recorded. Improvements have chiefly depended on the provision of materials not usually produced by the manufacturer of intermediate products. Thus the importance of fuming sulphuric acid became evident at a very early stage, and, later, alkylating agents, phosgene, formaldehyde, chlorine, acetic acid, chloroacetic acid, etc., became of increasing value. Chlorine, particularly, has of recent years been much used for the production of chlorinated nitrobenzenes, which are required for the manufacture of diphenylamine derivatives, and of nitrophenols, so much used for obtaining sulphide dyes.

Great attention has been paid of late to the production of anthraquinone derivatives which have proved to be readily convertible into vat dyes, and the gradual provision of further pure products of coal-tar, such as carbazole and acenaphthene, has widened the field of operations.

A general tendency is to be noticed in the direction of the increased use of catalytic agents. Even in the early days of the industry it was found, for example, that the presence of a small amount of benzoic acid was necessary for the production of the finest aniline blues, and the employment of mercury in the preparation of phthalic acid and, more recently, in directing the mechanism of the sulphonation of anthraquinone is well known. Many other substances have been used, among which may be mentioned iodine, iron, vanadium, copper, and several of the rare metals or their oxides.

It is not too much to hope that many operations that are now carried out by means of energetic chemical agents may, in the future, be brought about in a much simpler manner by the agency of catalysts. One may confidently expect that, in order simply to convert a hydrogen atom in the benzene ring into hydroxyl, instead of the cumbrous process of sulphonation followed by fusion with alkali, air and a catalyst will be made to produce the same effect.

Electrical energy, also, has been brought under the sway of the chemist, particularly in connexion with oxidation and reduction. Although not yet in very extended use in organic chemistry, it will no doubt in the future play a great part in the preparation of intermediate products.

The chief chemical reactions which are employed for the manufacture of intermediate products are few in number compared with the vast quantity of materials which are now available for the dye manufacturer. They may be briefly enumerated as follows :

Nitration.—Effected generally by a mixture of the theoretical quantity of nitric acid with sulphuric acid ; in a few cases nitrous gases or sodium nitrite in acid solution are used. In the case of amines, these must be protected from the oxidising action by acylation, the acyl group being subsequently eliminated.

Nitrosation.—The nitroso-group is introduced into a tertiary amine by treatment with nitrous acid (sodium nitrite in acid solution).

Halogenation.—Brought about by direct treatment with chlorine, bromine, or iodine ; also by these elements in the nascent condition (sodium hypochlorite and acid), sometimes by sulphuryl chloride, phosphorus chlorides, etc. Here again, amines must first be acylated.

Sulphonation.—Generally by the action of sulphuric or fuming sulphuric acid. Sometimes by chlorosulphonic acid, and sulphurous acid (bisulphites). The influence of traces of mercury is strikingly illustrated in the case of the anthraquinonesulphonic acids.

Reduction—(a) to the amino-group.—With iron and a little hydrochloric, sulphuric, or acetic acid, sometimes with zinc and hydrochloric or sulphuric acid, and with sodium hyposulphite (hydrosulphite) in neutral or faintly alkaline solution; the latter method is particularly useful in reducing azo-compounds. Occasionally with sodium hydrogen sulphite.

(b) To the azoxy-, azo-, and hydrazo-groups.—With zinc and an alkali hydroxide.

Electrolytic reduction is also sometimes employed.

Oxidation.—Energetic oxidation is brought about by chromic or nitric acid. Milder oxidation is effected by fuming sulphuric acid, manganic sulphate, manganese dioxide, chlorine, or permanganate.

Electrolytic oxidation is also occasionally used.

Fusion with alkali.—Sodium hydroxide is almost invariably employed, although in certain cases the use of potassium hydroxide is preferable. In fusions in open pans, sodium hydroxide is melted with the addition of a little water ; when the operation is conducted in autoclaves, a solution is employed.

Hydrolysis.—By heating with acids or alkalis of various strengths.

Amidation.—In cases where an amino-group cannot be introduced by reducing a nitro-group, amidation is effected by heating with concentrated aqueous ammonia ; the presence of a sulphite is of great advantage.

Alkylation.—By means of methyl or ethyl alcohol, or of the alkyl alkali sulphates or alkyl sulphates, more rarely by the alkyl haloids. Occasionally formaldehyde may be employed (followed by reduction) and chloroacetic acid (followed by elimination of carbon dioxide from the condensation product). *Arylation* is usually effected by means of the corresponding amine.

Acylation.—The introduction of acid radicles is brought about by means of acetic or formic acids, acetic anhydride, benzoyl chloride, *p*-toluenesulphonyl chloride, etc.

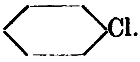
Condensation.—Important condensing agents are carbonyl chloride (phosgene), formaldehyde, aluminium chloride, ferric chloride, iodine, etc.

Although the chemical engineering, as well as the chemistry, of the processes described in this book has not been lost sight of, the object and scope of the work do not permit of full engineering details being given. The scale of manufacturing adopted will, of course, be an important factor in deciding on the size of plant, but in any case it will be found extremely useful, if not necessary, to attach to the works laboratory a large room (or rooms) fitted up with small scale plant made in the same way as that to be used in the works. Having worked out any particular process in the laboratory (see Chapter XXVI, " The Technical Laboratory," Cain and Thorpe, " Synthetic Dyestuffs "), the chemist will then transfer his operations to the small scale plant. This should be of such a size that the chemist and his assistants can conveniently handle the materials dealt with. For this purpose, sulphonation pans, enamelled nitration pans, and fusion pans (with outlet) should be of 3–5 gallons capacity. Reduction pans of 10–15 gallons, tubs and receivers of 20–30 gallons, and autoclaves of 2–4 gallons capacity (fitted with stirrers, and glass, enamelled iron, lead, and ferro-silicon linings, and tested to 100 atmospheres for ammonia or 20 atmospheres for low pressures), should be provided, and the equipment should include vacuum filters, filter presses, evaporating plant, centrifuge, vacuum still, hydraulic press, vacuum drier, grinders and mills, simple enamelled iron pans (5–10 gallons) which can be moved about and serve to collect filtrates, etc., earthenware pans, etc. In addition, a system of water, steam, compressed air, gas, and vacuum pipes will be necessary, as well as power to drive the stirrers.

With such a plant, assembled in a suitable manner on the floor and one or more stages so as to use gravity as much as possible for transporting liquids, the chemist will be enabled to work out his processes in a really technical fashion, and should find much less difficulty in transferring them to the works scale than if he had been content to work in the glass and porcelain of the ordinary laboratory.

BENZENE SERIES

CHLORO- AND CHLORONITRO-DERIVATIVES

CHLOROBENZENE, 

The chlorination of benzene is carried out by passing a stream of chlorine through benzene in the presence of a catalyst. Iron is used on the large scale, but other catalysts, such as iodine, molybdenum pentachloride, vanadium tetrachloride, aluminium chloride, and the aluminium-mercury couple, have been employed in the laboratory.

In this reaction some dichlorobenzene is also produced (mostly *p*- with a little *o*-), and in order to keep the quantity of this as low as possible the temperature must be regulated, and a deficiency of chlorine is employed so as to leave an excess of benzene at the end of the operation. In practice, about 60 per cent. of the theoretical yield can be obtained in one operation, from which, however, the excess of benzene is recovered and can be chlorinated afresh. For monochlorination, 78 parts of benzene require 71 parts of chlorine; instead of the latter amount, 40 parts of chlorine are used, corresponding with an increase in weight of the benzene of 20 parts (the other 20 parts passing off as hydrochloric acid).

The following table gives the results of three experiments made in the presence of 0·5 per cent. of iron at a temperature not above 40° (Grandmougin, *Rev. prod. chim.*, 1917, **20**, 216).

	1	2	3
Benzene	80	80	80
Increase in weight to	89	97	118

Fractionation gave the following result:

Boiling up to 100°	60	35	—
„ 100–120°	6	25	—
„ 120–140°	23	28	50
„ above 140°	—	—	60
Residue	—	9	8
	89	97	118

(The boiling points of the pure materials are: benzene, 80·5°; chlorobenzene, 132°; *p*-dichlorobenzene, 174°.)

Refractionation of the products of the second experiment gave 35 parts of benzene, 10 parts of partly chlorinated benzene, 40 parts of chlorobenzene, b. p. 128–134°, and 5–10 parts of dichlorobenzene. It will be seen that the third experiment gave a considerable amount of dichlorobenzene.

An experiment with the aluminium-mercury couple, in which 50 grams of benzene were mixed with 0·5 gram of the couple (Cohen and Dakin, *Trans.*, 1901, **79**, 1111) and cooling effected by means of ice, gave the following results (for the purpose of comparison the quantities are calculated for 80 parts of benzene):

Benzene	80
Increase in weight to	101

Fractionation gave the following result:

Boiling below 127°	6·4
„ 127–137°	80
„ 137–160°	8
„ above 160°	6·4
	100·8

In this experiment the amount of crude monochlorobenzene corresponds with about 70 per cent. of the theoretical yield.

A chlorination plant described by Marckwald (E.P., 17695 of 1902; F.P., 328053; G.P., 142939; U.S.P., 721961) is shown in Fig. 1.

The benzene is contained in a still, 1, fitted with a fractionating column, 2, leading to a condenser, 3, from which, through a cooling coil, 4, the benzene is brought through to the chlorinating vessel, 6, at the temperature desired. The stream of chlorine from a cylinder of the liquefied gas entering at 7 is so adjusted that excess of benzene is always present, and the hydrochloric acid formed passes away through a pipe, 8, at the top of the chlorinating vessel. When the liquid in the latter has reached a certain height it automatically runs back to the still through 9. The flow of benzene to the chlorinating vessel is regulated so as to correspond with the flow of liquid back to the still. The contents of the still continually become richer in chlorobenzene, and this is retained there by the action of the fractionating column, which allows only benzene to reach the chlorinating vessel. As the capacity of the chlorinating vessel is considerably less than that of the still, nearly the whole of the benzene is transformed into chlorobenzene, and when this is effected the contents of the still are run off through 10 to be neutralised and fractionated.

According to G.P., 219242* (Saccharinfabrik, Aktiengesellschaft vorm. Fahlberg, List & Co.), if a mixture of ferric chloride and iron is used as catalyst the reaction proceeds very smoothly and without appreciable increase in temperature, so that cooling is not required. The stream of chlorine is stopped before all the benzene is chlorinated so as to lessen the possibility of the formation of the dichloro-compound. The vessel in which the operation is conducted is connected with the vacuum pump and the contents are distilled, the outside temperature being 80°. Hydrochloric acid and chlorine first pass off and then benzene. The chief fraction is chlorobenzene, containing a very small amount of dichlorobenzene. The catalyst remains behind and can be used again, whilst the benzene is put back and re-chlorinated. Alternatively, the whole distillate can be collected and then fractionated under the atmospheric pressure. In this way 300 kilos. of benzene were treated with 1 kilo. of ferric chloride and 1 kilo. of iron powder, and 156 kilos. of chlorine

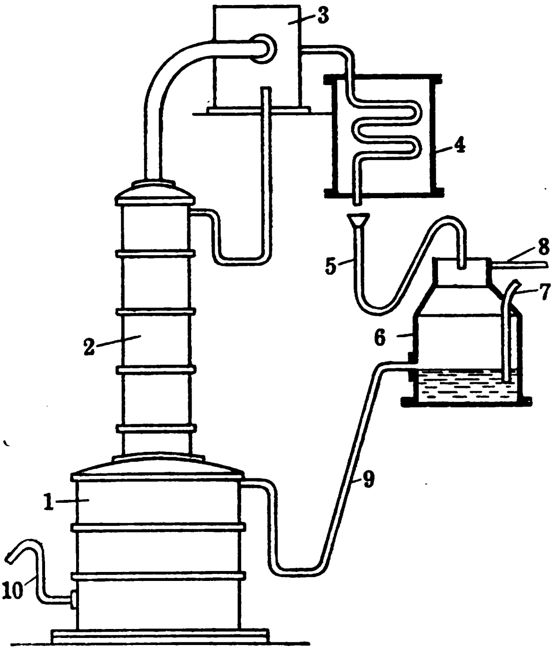


Fig. 1.

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* This patent was allowed to expire in the year in which it was taken out (1910).

led in. There were obtained 205 kilos. of chlorobenzene (b. p. 131–133°) and a first running of 145 kilos. of a mixture of benzene and chlorobenzene which, when treated with 30 kilos. of chlorine, gave 90 kilos. of chlorobenzene and a first running of 55 kilos., from which 30 kilos. of chlorobenzene were produced. The total yield from 300 kilos. of benzene was 335 kilos. of pure chlorobenzene, 24 kilos. of pure *p*-dichlorobenzene, and 13 kilos. of a mixture of chlorinated benzenes. The amount of chlorine used was 230 kilos., and 115 kilos. of hydrochloric acid gas (= 380 kilos. of 30 per cent. hydrochloric acid) were recovered.

The preparation of the catalyst in a special way is the subject of a patent by Rabinovitz (U.S.P., 1189736). The catalyst is prepared by mixing equal weights of iron, reduced by hydrogen, and ferric chloride (containing $6H_2O$). These are thoroughly triturated in a mortar, when at first liquefaction takes place; but, on keeping, a rise in temperature occurs and the mass becomes solid. This is ground to pass a 100-mesh sieve and then carefully dried. A sub-chloride is said to be produced in this way.

Chlorination is effected in tall tanks fitted with an agitator shaft carrying paddles and equipped with a cooling coil or jacket.

Two hundred parts by weight of benzene and 2 parts of the above catalyst were subjected, with agitation, for four hours to a current of dry, air-free chlorine, the temperature being maintained between 10° and 15°. No chlorine escaped, as absorption was complete. The product was washed, dried, and distilled, and consisted largely of chlorobenzene.

Instead of washing the chlorobenzene it may be distilled directly and the dissolved hydrogen chloride partly liberated, whilst any unchlorinated benzene saturated with hydrogen chloride may be returned to the chlorinating vessel.

Coutagne (F.P., 480151) arranges the chlorination process so that fresh chlorine comes into contact with fresh benzene. A stream of benzene flows through a vertical series of basins exposed to a stream of chlorine passing in the same direction as the benzene. The formation of higher chlorinated derivatives is further reduced by mixing with the chlorine hydrochloric acid previously formed in the reaction. Iron is used as the catalyst and the benzene is maintained at 15°.

A continuous process for the chlorination of benzene is described by Auger (E.P., 100105 [1916]; F.P., 482372; U.S.P., 1180964). From the reservoir (Fig. 2) at the highest point benzene is fed into a lead-lined water-jacketed cylinder, 1, filled with siliceous pebbles so as to present a large surface of benzene to the action of the chlorine which enters the cylinder from below. The flow of benzene is regulated so as completely to absorb the chlorine, this operation being controlled by means of the indicator, 5. The solution of chlorine in benzene enters the bottom of a cast-iron cylinder, 2, placed below the first one, also cooled externally and filled with iron borings. The solution gradually rises in this cylinder and, in contact with the iron, the reaction takes place, hydrochloric acid gas passing off through the top of the cylinder. When the chlorobenzene has reached a certain height in the cylinder it overflows through a connecting pipe to the washer, 3, where it is neutralised with moist chalk, and then passes through the container to the still, 4, where it is fractionated. According to the patentee, the product contains about 30 per cent. of chlorobenzene, and the proportion of chlorobenzene to polychlorinated products is about 100 : 6. This apparatus is used in France and in Italy.

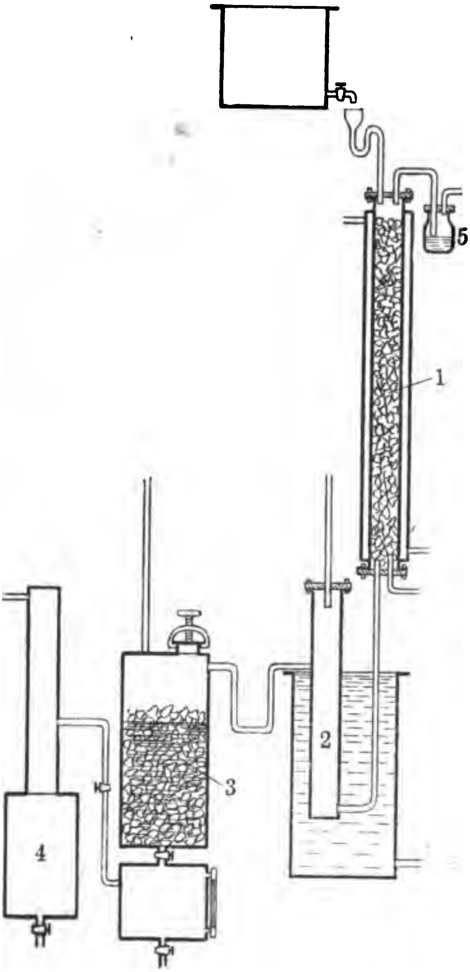


Fig. 2.

The chlorination may also be effected with nascent chlorine, thus according to the Société Chimique des Usines du Rhône

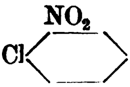
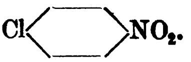
(F.P., 479645) 200 kilos. of benzene, 100 kilos. of manganese dioxide, and 400 kilos. of hydrochloric acid are heated together to a temperature just below the boiling point of benzene. When the reaction is finished the chlorobenzene is separated from the aqueous solution of manganese chloride and the excess of benzene distilled off.

Pure chlorobenzene is a colourless liquid with a faint aromatic odour, b. p. 132°. D$^{20}_{4}$ 1·10601, D^{0} 1·12786. The technical product boils at 131–133° and has D^{15} 1·108.

p-Dichlorobenzene melts at 53° and boils at 174°.

It is estimated (Grandmougin, *loc. cit.*) that about 10,000 tons of chlorobenzene are manufactured yearly, of which about 6,000 tons are used for the production of sulphur blacks. The same author gives, for the purpose of calculating the cost of manufacture, the following figures: 100 kilos. of benzene and 75 kilos. of chlorine furnish 100 kilos. of chlorobenzene and 100 kilos. of hydrochloric acid of 30 per cent. strength.

Chlorobenzene is used for the manufacture of *o*- and *p*-chloronitrobenzene and chlorodinitrobenzene.

o- and p-CHLORONITROBENZENES,  *and* 

When chlorobenzene is nitrated a mixture of *o*- and *p*-chloronitrobenzene is obtained, together with a minute quantity of the meta-compound. Holleman (*Rec. trav. chim.*, 1900, **19**, 188) added 25 grams of chlorobenzene at 0° to a mixture of 50 c.c. of yellow nitric acid (D 1·48) and 10 c.c. of yellow nitric acid (D 1·52). The product was washed with ice-water, melted, and dried at 120°. The solidifying point was 58·9°. This consisted of 30·1 per cent. of *o*- and 69·9 per cent. of *p*-chloronitrobenzene. When the nitration was carried out at —30° the proportions were 26·9 and 73·1 per cent. respectively.

In a later paper (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, **7**, 266) Holleman gives the proportions, obtained by nitrating at 0°, as 29·8 per cent. of *o*-, 69·9 per cent. of *p*-, and 0·3 per cent. of *m*-chloronitrobenzene. He estimated the relative quantities of *o*- and *p*-compounds by means of a table of solidifying points of mixtures of the two, and as this table is of much value in determining the composition of the various fractions obtained in the separation, it is reproduced here.

Solidifying Points of Mixtures of o- *and* p-*Chloronitrobenzenes.*

Per cent. of para.	Solidifying point.	Per cent. of para.	Solidifying point.
0	32·09°	35·43	18·43°
1·05	31·06	37·53	21·9
4·60	29·92	39·96	26·10
6·54	29·00	41·67	28·50
8·88	27·89	45·86	33·98
12·61	26·10	48·94	37·65
16·26	24·19	60·18	50·1
19·22	22·65	64·66	54·32
22·91	20·75	68·54	57·83
26·89	18·30	70·02	59·22
30·26	16·29	71·93	60·80
32·39	15·35	75·48	63·97
32·71	14·94	81·93	69·10
32·90	14·85	86·70	72·77
33·07	14·77	90·30	75·40
33·1	14·65	95·57	79·13
34·09	16·73	100	82·15
34·94	17·47		

The eutectic point is thus at 14·65° with a mixture composed of 33·1 per cent. of *p*- and 66·9 per cent. of *o*-chloronitrobenzene. From a curve constructed from the above figures, ordinates being temperatures and abscissæ percentages of the *p*-compound, it is easy to read off the amount of *p*-compound corresponding with any observed solidifying point.

The separation of the two isomerides is effected by a combined process of crystallisation and distillation. According to the Chemische Fabrik Griesheim (E.P., 2480 of 1898; G.P., 97013), after crystallising out the *p*-compound, about equal quantities of *o*- and *p*-compounds are left. Of this liquid mixture, 1,000 kilos. are fractionated in a good fractionating apparatus either under ordinary pressure using direct heat or under diminished pressure with indirect steam. The first fractions, on cooling, give a first crystallisation of pure *p*-chloronitrobenzene, and the last fractions give a similarly pure *o*-compound which is freed from adhering liquid by means of a centrifuge. On further cooling, the second crystallisations yield the para-compound containing ortho and the ortho-compound containing para respectively. The corresponding fractions of the distillation and crystallisation are collected and the still impure fractions, when they amount to 1,000 kilos., are again fractionated. By systematic distillation and crystallisation it is finally possible to separate the two isomerides completely.

Marckwald (G.P., 137847) separates the crude mixture of *o*- and *p*-chloronitrobenzenes as follows: The mixture is cooled to 16°, when some of the *p*-compound crystallises out, whilst by further cooling a mixture containing 21 parts of the *o*- and 10 parts of the *p*-compound separates. One hundred kilos. of this mixture are stirred with 50 litres of alcohol (80 per cent. by volume) at 33°. After settling, the excess of the liquid mixture of *o*- and *p*-chloronitrobenzenes is drawn off, dried, and cooled to 16°, whereby 0·9 kilo. of the *p*-compound (m. p. 83°) crystallises out and is filtered off.

From the alcoholic solution the alcohol is distilled off, and the remaining mixture of *o*- and *p*-compounds is separated from water, cooled to 16°, and filtered from about 1·8 kilos. of *o*-chloronitrobenzene (m. p. 32·5°). The liquids remaining from both crystallisations are again treated with alcohol. The degree of dilution of the alcohol must be such that the liquid mixture of the *o*- and *p*-compounds is not entirely dissolved.

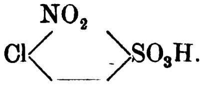
The melting and boiling points of the three chloronitrobenzenes are given below.

	m. p.	b. p. 753 mm.	b. p. 8 mm.
Ortho	32·5°	245·5°	119°
Meta	44·4	235 6	—
Para	83	238·5	113

o-Chloronitrobenzene is used for preparing *o*-nitroanisole (by the action of dilute methyl alcohol in the presence of sodium hydroxide) which leads to *o*-anisidine and dianisidine.

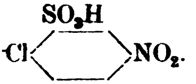
p-Chloronitrobenzene is used for the preparation of substituted diphenylamines which are employed in the manufacture of sulphur dyes.

4-CHLORO-3-NITROBENZENESULPHONIC ACID,



o-Chloronitrobenzene is added to 5 parts of fuming sulphuric acid (containing 30 per cent. of sulphur trioxide) and the mixture heated on the water-bath until no oil separates on pouring a sample into water. (If *p*-chloronitrobenzene is present it is not attacked, and crystallises out in this test.) About six hours' heating is required. The solution is then poured into cold water, and if any of the para-compound is present it will crystallise out. The filtrate from this is neutralised with milk of lime, the calcium sulphate filtered off, the calcium salt converted into sodium salt, and the solution evaporated (Fischer, *Ber.*, 1891, **24**, 3186). The free acid crystallises with $1H_2O$. It is used for making aniline-2 : 5-disulphonic acid.

2-CHLORO-5-NITROBENZENESULPHONIC ACID,

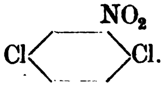


p-Chloronitrobenzene is added to 6 parts of fuming sulphuric acid (containing 10–12 per cent. of sulphur trioxide) and the mixture is heated at 120–130° until a sample dissolves in dilute alkali. The mixture is poured into water, neutralised with milk of lime, the calcium sulphate filtered off, and the solution of the calcium salt converted into sodium salt by sodium carbonate. After filtering from calcium carbonate the solution is evaporated (Claus and Mann, *Annalen*, 1891, **265**, 87; compare Fischer, *Ber.*, 1891, **24**, 3185).

Ullmann and Jüngel (*Ber.*, 1909, **42**, 1077) heated 157·5 grams of *p*-chloronitrobenzene with 200 c.c. of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide) for 6 hours at 160° and poured the cooled mixture on 425 grams of ice. The sulphonic acid crystallised out and, after being collected and washed with a little dilute sulphuric acid, was dissolved in water and steam was passed through the solution, driving off 0·6 gram of unchanged *p*-chloronitrobenzene. The pure acid separated from the solution, especially on adding fuming hydrochloric acid. The yield was 246 grams or 91 per cent. of the theoretical.

The acid crystallises from water with $2H_2O$; the sodium salt with $1H_2O$. It is used for making 4-nitroaniline-2-sulphonic acid.

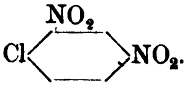
2 : 5-DICHLORONITROBENZENE,



p-Dichlorobenzene is readily converted into 2 : 5-dichloronitrobenzene on nitration with 1·5 parts of a mixture containing 2 parts of nitric acid (D 1·54) and 3 parts of concentrated sulphuric acid. After mixing the reagents together at the ordinary temperature, the reaction is finished on the water-bath (Morgan and Norman, *Trans.*, 1902, **81**, 1382).

2 : 5-Dichloronitrobenzene melts at 54·5° and boils at 266°. It is used for making 2 : 5-dichloroaniline.

4-CHLORO-1 : 3-DINITROBENZENE,



This is obtained by nitrating *p*-chloronitrobenzene with a mixture of nitric and sulphuric acids or by adding gradually chlorobenzene to 5–6 times its weight of sulphuric acid mixed with two molecular proportions of sodium nitrate. The temperature is raised to 80–90° to complete the reaction and the product poured into water. The dinitro-compound is remelted with boiling water to free it from acid. The yield is almost theoretical (Einhorn and Frey, *Ber.*, 1894, **27**, 2457).

The technical details are described by Ellis (U.S.P., 1220078) as follows:

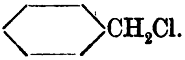
About 2 parts by weight of sodium nitrate and 6 parts of sulphuric acid (66° Bé.) are mixed together in a nitrating pan fitted with a stirrer, with heating and cooling coils or jacket, and are stirred until the sodium nitrate is practically all in solution. One part of chlorobenzene is then added slowly while the mixture is cooled, the temperature not being allowed to rise above 100°. After all the chlorobenzene has been added, the temperature is kept at 100° for several hours, and it is then gradually raised until at the end of about 15 hours the temperature has reached about 125°. Nitration is carried on at this temperature until the process is complete, which will require about 24 hours. During this operation the control of temperature may be best observed by watching the yellowish to reddish fumes given off from the mixture. If properly conducted, at no time should there be a copious evolution of nitrous fumes, and this may be conveniently observed by means of a sight glass fitted into the vent pipe from the nitrating pan. When the operation is complete the contents of the pan are allowed to settle, the lower layer of acid is drawn off, and the top layer is run into water which is well stirred. The granulated chlorodinitrobenzene is remelted with water so as to wash it free from acid, granulated again, and collected in a centrifuge.

Ostromisslenski, who nitrated *o*-chloronitrobenzene (*J. pr. Chem.*, 1908, [ii], **78**, 260), obtained an 80–85 per cent. yield of the theoretical and showed that a little 2-chloro-1 : 3-dinitrobenzene (m. p. 38°) was also formed in the reaction.

4-Chloro-1 : 3-dinitrobenzene melts at 51° and boils at 315°. Great care must be taken in handling it, as it attacks the skin.

It is used mostly for making dinitrophenol, but also for the preparation of substituted diphenylamines.

BENZYL CHLORIDE,



This is manufactured by passing chlorine into toluene contained in an acid-proof vessel and heated to boiling by means of a leaden steam-coil. The operation is interrupted when the toluene has increased in weight by the theoretical amount (37·5 per cent.). The vapours are condensed by means of a reflux coil and the escaping hydrogen chloride is passed into water. The product is washed with weak alkaline water and then rectified, by which means it is freed from unchanged toluene and higher chlorinated products (see the plant described under benzylidene chloride p. 19). In order to avoid the production of higher chlorinated products, Marckwald (E.P., 17695 of 1902; F.P., 328053; G.P., 142939; U.S.P., 721961) uses a plant in which the finished chloro-compound is constantly removed from the action of the chlorine.

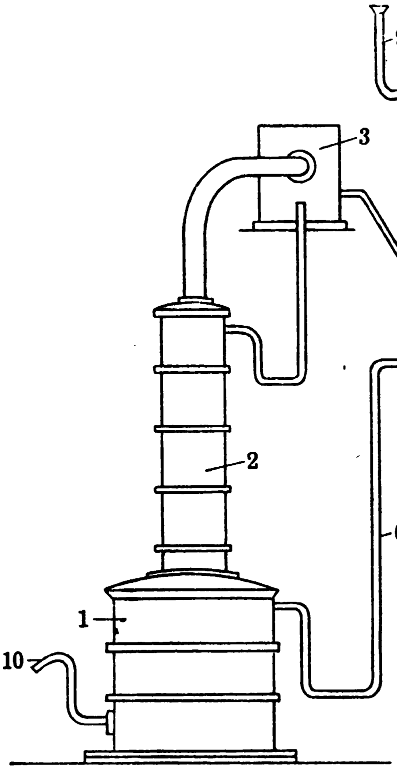


FIG. 3.

In the still 1 (Fig. 3), is placed a suitable amount of toluene, say 50 kilos., and about 0·5 kilo. of phosphorus trichloride, and the mixture is heated until the vapours of toluene enter through the column 2, and the condensing apparatus 3, into the vessel 4, in which the reaction takes place, and from 4 into the reflux condenser 5, in which the vapours are condensed. The toluene returning fills the vessel 4, being maintained at the boiling point by the toluene vapour. When the level of the toluene reaches a certain height in 4 it returns through the pipe 6 to the still 1. Chlorine is now introduced into the toluene by means of the pipe 7, until a thermometer placed in the condensing apparatus 3 shows a temperature above the boiling point of toluene, namely, 111°, and indicates that the chlorination of the toluene to be treated has been finished, so that the contents of the still 1 consist almost entirely of benzyl chloride. The hydrochloric acid gas escapes through 8. Through the pipe 9 is now introduced an amount of toluene equivalent to the amount of chlorine introduced at the same time into the apparatus. This fresh toluene is mixed with that contained in 4 and is vaporised with it and chlorinated, and the still 1 is continually fed with benzyl chloride, which flows away through the pipe 10. The product obtained in this way is purified by fractional distillation. The liquid from the vessel 4 may also be introduced into 1 through the column 2, thus economising fuel.

Wohl's process is as follows (G.P., 139552): A mixture of 200 kilos. of toluene and 180 kilos. of sulphuryl chloride is gently heated under a reflux condenser to about 103°, or the sulphuryl chloride can be run gradually into the gently boiling toluene. The hydrogen chloride which is evolved is led into fuming sulphuric acid to form chlorosulphonic acid, from which sulphuryl chloride is obtained. The sulphur dioxide is led away to the sulphuric acid plant. The temperature of the mixture should not rise above 110°, and when hydrogen chloride ceases to be evolved the sulphuryl chloride has all been used. The mixture is fractionally distilled, when rather more than half the toluene is regained and an almost theoretical yield of benzyl chloride is obtained, calculating on the toluene entering into reaction.

A process for chlorinating toluene in the presence of phosphorus trichloride by the aid of ultra-violet light has been patented by Ellis (U.S.P., 1146142, 1202040; compare also Du Pont de Nemours Powder Co., E.P., 879 of 1913; and Gibbs and Geiger, U.S.P., 1246739); and Conant (U.S.P., 1233986) obtains benzyl chloride by treating a mixture of toluene and bleaching powder with sulphur dioxide.

A study of the chlorination of toluene has been made by Cohen and his pupils (*Trans.*, 1905, 87, 1034; 1910, 97, 1623).

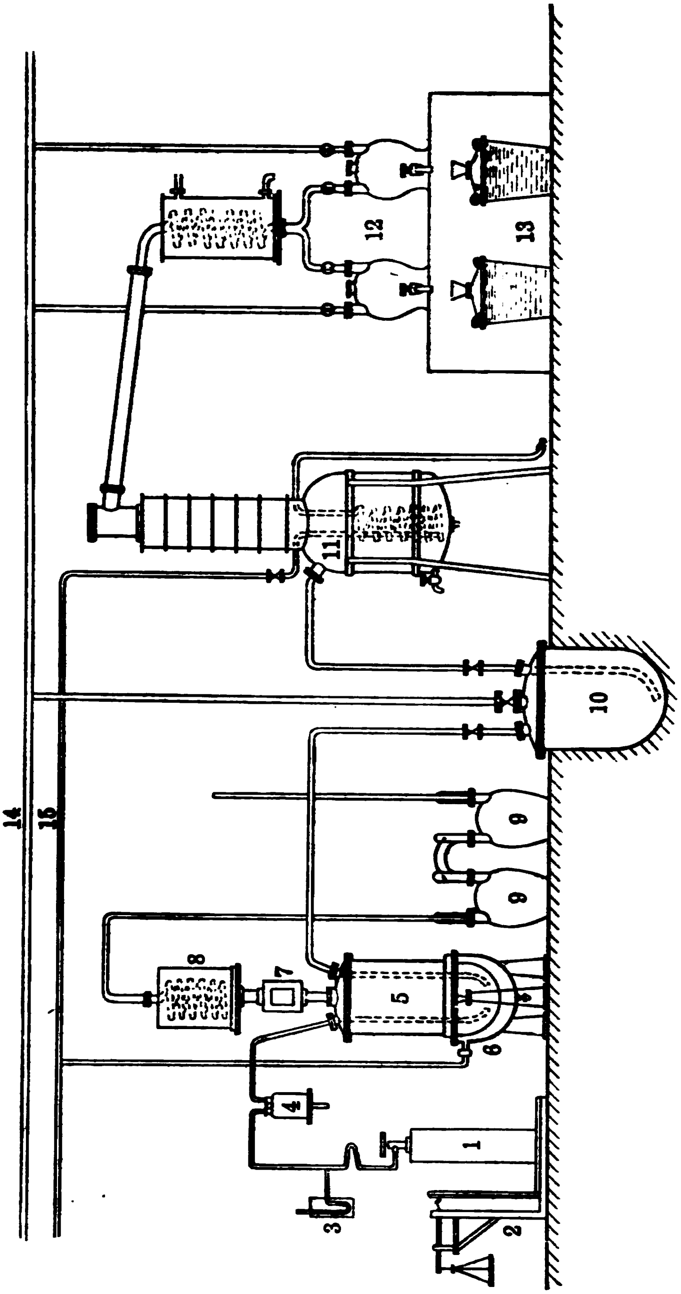


FIG. 4.

Benzyl chloride boils at 176° and has D^{0}_{4} 1·1135, D^{15}_{15} 1·1040, and D^{25}_{25} 1·0967. It is used for making benzylethylaniline, etc.

BENZYLIDENE CHLORIDE, (BENZAL CHLORIDE)

$CHCl_2$.

This is prepared by chlorinating benzyl chloride in Marckwald's plant (see p. 16) or by chlorinating toluene to the required stage in the apparatus shown on p. 18 (Grandmougin, *Rev. prod. chim.*, 1917, **20**, 296).

In the figure, 1 is a cylinder of liquid chlorine; 2, scales for controlling the amount of chlorine used; 3, a manometer; 4, control gauge; 5, chlorinating vessel surrounded by a steam-jacket, 6; 7, box with glass sides to admit light; 8, condenser; 9, jars to condense hydrochloric acid; 10, pressure pan or montejus; 11, still and column; 12, receivers; 13, containers for the product; 14, vacuum pipe; 15, steam pipe.

The chlorinating vessel is heated by steam or by an oil-bath; the condenser returns the liquid to the vessel and allows the hydrogen chloride to pass over and be condensed in the earthenware jars. A little phosphorus trichloride is used to act as a catalyst.

As the stream of chlorine can be stopped at any desired point, the apparatus can be used for obtaining either benzyl chloride, benzylidene chloride, or benzotrichloride. In preparing benzyl chloride, the vacuum fractionating apparatus serves to separate this product from unchanged toluene. In making benzylidene chloride, the fraction distilling below 200° or at the temperature corresponding with the vacuum is collected.

The apparatus must be constructed with materials not attacked by chlorine, such as earthenware, lead, or ferro-silicon.

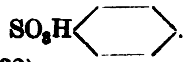
Chlorine is passed into the boiling toluene until the density has risen a little above that of benzylidene chloride (1·2557 at 14°; it is also given as 1·295), and the product, which contains some benzotrichloride, is used direct for making benzaldehyde. One hundred kilos. of toluene and 180 kilos. of chlorine give 160 kilos. of crude benzylidene chloride.

Benzylidene chloride boils at 206° and has D^{14} 1·2557, whilst benzotrichloride boils at 213–214° and has D^{14} 1·38.

A rapid technical method of estimating mixtures of the three chloro-derivatives is described by Lubs and Clark (*J. Amer. Chem. Soc.*, 1918, **40**, 1449).

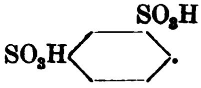
BENZENESULPHONIC ACIDS.

BENZENESULPHONIC ACID,



See under Phenol, p. 104 (also p. 132).

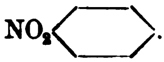
BENZENE-*m*-DISULPHONIC ACID,



See under Resorcinol, p. 130.

NITRO-COMPOUNDS.

NITROBENZENE,



The usual arrangement now adopted (*Chem. Trade J.*, 1906, 38, 59) is as illustrated on p. 21.

The nitration pan 6 (Fig. 5), has a total capacity of 1,600 gallons and is made of cast iron 1¼ inches thick, the sides, from the lid down to a depth of 3 feet, being ¼ inch thicker. The vertical agitating shaft is suspended from the lid on ball bearings and carries two propeller agitators. The internal cooling-pipes 9 consist of two separate coils of thin pure chemical lead without flaw, 2 inches in diameter, each coil being about 150 feet long. They are supported on circular cast iron grates or tables as shown, and are spaced out so as to allow free passage of the liquid between them. The vertical portions, connecting the coils with the exterior, should be protected, as these are quickly attacked. This is done by threading them through lead pipes of slightly larger diameter, and filling up the intervening space with acid-proof cement.

To direct the upward flow of the liquid, the lower propeller agitator is surrounded by a cast iron cylinder with large perforations at the bottom to admit the descending liquid. This serves also as a support for the grates and coils.

The other vessels used, viz., the mixed acid pan 1, the nitrobenzene wash-pan 17 (1,000 gallons capacity), and the egg 23, are also made of cast iron. In addition, a wrought iron measure tank for benzene (to measure 500 gallons) is fixed outside the building on about the same level as the mixed acid pan 1. This measure tank is not shown in the diagram.

Method of Working.—From the benzene store tank benzene is blown by compressed air into the benzene measure tank (outside the nitrobenzene building) and the flow stopped when 500 gallons are in. This is then run into the nitrating vessel 6.

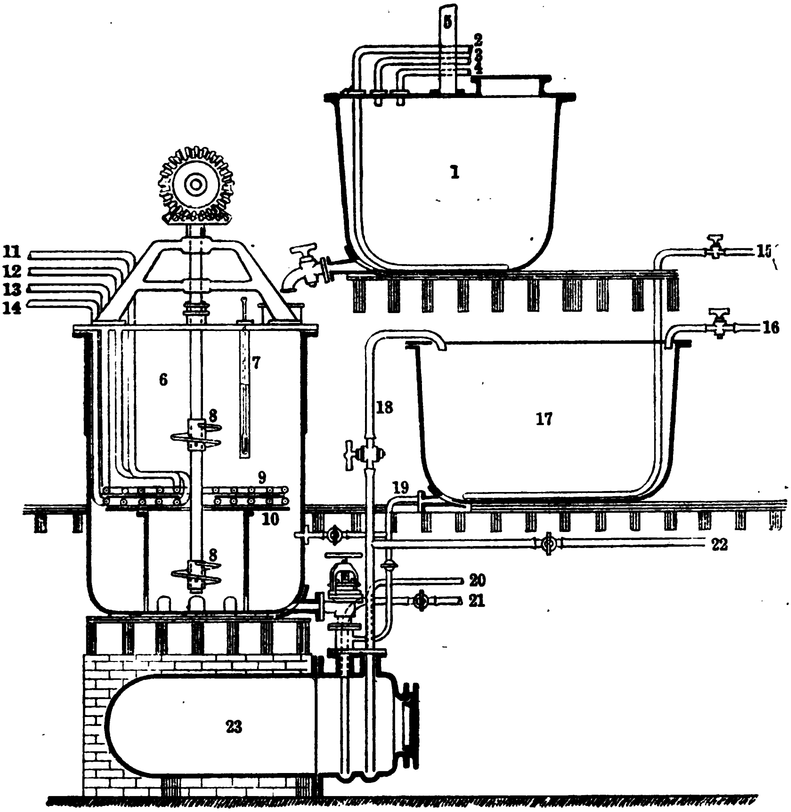


FIG. 5.

1. Mixed acid pan.
2. Compressed-air pipe.
3. Sulphuric acid inlet.
4. Nitric acid inlet.
5. Acid-vapour pipe.
6. Nitrobenzene pan.
7. Thermometer.
8. Propeller agitator.
9. Lead cooling coils.
10. Supporting grids.
11. Cooling-water outlet.
12. " " "
13. Cooling-water inlet.
14. " " "
15. Compressed-air pipe.
16. Water inlet.
17. Nitrobenzene wash-pan.
18. Pipe from egg.
19. Nitrobenzene pipe.
20. Compressed-air pipe.
21. Waste-acid pipe.
22. Pipe to nitrobenzene tank.
23. Air-pressure egg.

In the nitric acid store egg outside the building are put 5,000 lb. of nitric acid (D 1·43 or 86° Tw.; this is a suitable strength, but a corresponding amount of slightly weaker or stronger acid may be used) and in the sulphuric acid store egg (outside building) are similarly placed 6,600 lb. of sulphuric acid (96 per cent.). The nitric and sulphuric acids are now blown together into the mixed acid pan 1, and the two well mixed by turning on a current of compressed air through the pipe 2, which contains several holes in the straight part at the bottom of the pan. [Mixtures of the two acids may also be made in another part of the works and the right amount (decided by analysing the mixture) may be blown direct to the mixed acid pan.]

The mixed acid is run in a thin stream into the benzene while the agitators are revolving at a speed of about 60 revolutions per minute. The temperature is noted by means of the thermometer 7, which dips into the liquid and is protected by the metal tube (cast iron preferably). The temperature is allowed to reach 40–50° fairly soon (the nitration should not be carried on at too low a temperature, otherwise the nitric acid may not act very much on it, and, when the temperature rises, the reaction may suddenly start with explosive violence). Towards the end the temperature may be allowed to rise to 60°. The temperature is controlled by regulating the rate of flow of the mixed acids and also by the cooling water through the lead cooling coils. The running in of the mixed acids may take about eight hours, and after all is in the whole is kept stirring for about two to four hours or until no further rise in temperature is observed. A sample is taken and examined to see if the nitration is finished, shown by there being no benzene present.

The stirrer is now stopped, and the batch allowed to settle for two or three hours. The waste acid which will have settled to the bottom is run into the egg 23, and blown to the waste acid store tank to be concentrated. In order to see when all the waste acid has run out of the nitrator, a gap should be left immediately after the outlet from the nitrator so that the flow can be stopped as soon as nitrobenzene appears.

When the waste acid is drawn off the nitrobenzene is run into a second similar egg and blown into the wash-pan 17. Here it is washed twice with water (an equal volume each time) and mixed by means of a current of air blown through 17. Finally, it is washed with water containing sodium carbonate or sodium hydroxide enough to neutralise the remaining acid. After settling a few hours, the nitrobenzene is run into the egg 23, and blown to a store tank for nitrobenzene (not shown in the diagram) set sufficiently high to allow the nitrobenzene to run by gravity into the measure tank for the aniline reduction pan. The wash-water, which contains a little nitrobenzene in suspension, is run into a series of settling tanks, and the oil recovered. Although it is possible to work a charge of benzene in each machine daily, it is customary to have a duplicate set of machines, and to work each machine on alternate days. For an output of 150 tons of pure aniline oil per month, six nitrobenzene machines are required, with their corresponding adjuncts, as shown in the figure. The yield of nitrobenzene from the pure benzene employed is 154½ per cent. by weight, and this approaches so near the theoretical yield, namely, 157·6 per cent., that there is little room for improvement. It is possible slightly to increase this yield by settling the waste acid for forty-eight hours in a series of tanks, and skimming off the nitrobenzene, but in practice it has not been found to pay for the trouble, especially if the previous separation be carefully watched.

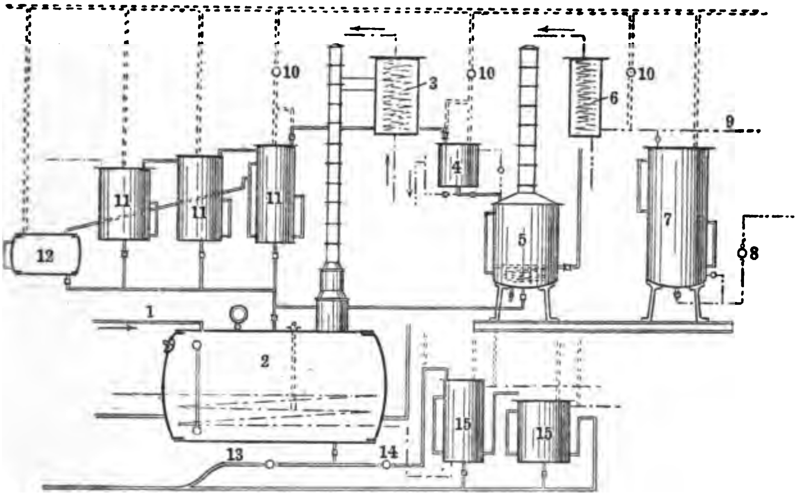


FIG. 6.—DISTILLATION OF NITROBENZENE IN A CURRENT OF STEAM.

1, Inlet for washed nitrobenzene (containing benzene); 2, still, with direct steam-pipe, cooling coils, thermometer, manometer, etc.; 3, condenser; 4, separator, for benzene and water; 5, still, for recovered benzene; 6, condenser for benzene; 7, store-tank, for recovered benzene; 8, pump and outlet pipe for benzene; 9, pipe leading to solvent naphtha store-tank; 10, alarm-thermometer to indicate insufficient cooling; 11, tanks for separating nitrobenzene and water after the benzene has been removed and the nitrobenzene condensed in 3; 12, store-tank for distilled nitrobenzene; 13, pipe for nitrobenzene, freed from benzene (but not distilled) leading to store-tanks; 14, pump for water and nitrobenzene; 15, tanks for separating nitrobenzene and water.

When the nitrobenzene is to be sold as "myrbane" it is distilled under diminished pressure, or in a current of steam, in order to obtain a perfectly clear and transparent liquid such as the users of myrbane demand. For this purpose it is customary to use one of the mixtures of benzene and toluene produced in the separation of these by fractional distillation. Fig. 6 shows an arrangement for distilling nitrobenzene in a current of steam.

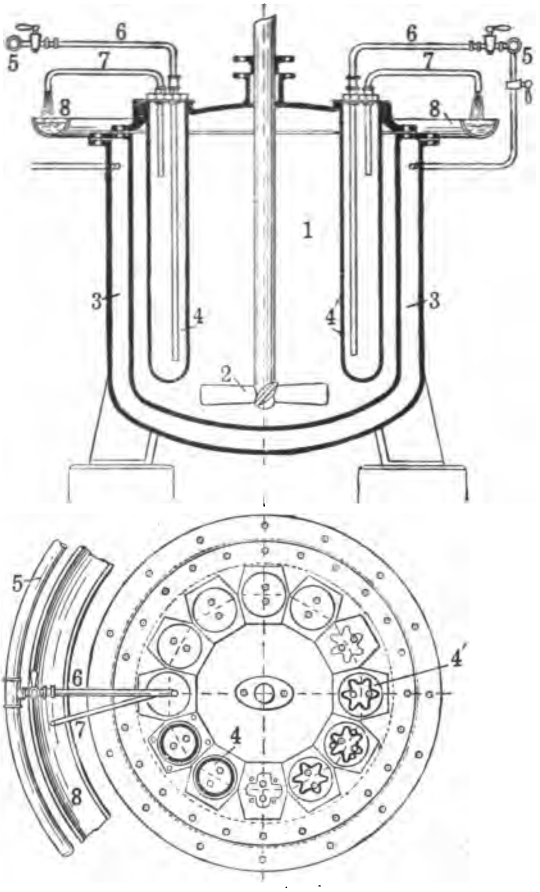


FIG. 7.

1. Nitrating pan.
2. Stirrer.
3. Water-jacket.
4 and 4′. Cooling tubes, round or corrugated.
5. Water supply.
6. Pipe leading water to bottom of tube.
7 and 8. Outlets for water.

The use of internal cooling coils, as described above, is attended with certain disadvantages, as these are apt to be corroded and leak. The nitrator is therefore often surrounded by a cooling jacket, and a water-cooled cylinder may also be placed inside the nitrator; the stirring arrangement is placed within this cylinder and the liquid is drawn into the cylinder at the top and emerges at the bottom (*Cotton*, 1916, **80**, 578).

Another cooling arrangement consists in fitting vertical cooling tubes in the lid of the nitrator, which is also jacketed (Fig. 7). Water is delivered to the bottom of these tubes and emerges through a siphon at the top (Eisenwerk Kaiserslautern, G.P., 244267). It is obvious, also, that the speed of the operation can be greatly increased by using the cold brine (or calcium chloride), from an ice-machine instead of cold water.

It is the modern custom to employ propeller or turbine agitators running at a very high speed (120–140 revolutions per minute).

Another arrangement of a nitrobenzene plant is shown in Fig. 8 (Grandmougin, *Rev. prod. chim.*, 1916, **19**, 346).

The fact that several explosions have occurred in nitrobenzene plants, owing probably to the mixed acids being run into the benzene without the agitator being started, and then, on starting the stirrer, great heat being developed on the sudden mixing of benzene and nitrating acid (notably a disastrous explosion in the works of the Aktiengesellschaft für Anilinfabrikation at Rummelsburg in 1914), has led to the introduction of automatic, continuous nitrating plants.

Fig. 9 shows a continuous nitrator used by the Westfälisch-Anhaltische Sprengstoff-Aktiengesellschaft (G.P., 274854; described by Neumann, *Chem. Ind.*, 1914, **37**, 337).

1 is the nitrator containing, on the inside walls, projections *a*, between which corresponding projections *b*, on the cylindrical stirrer 2, revolve. The two liquids to be mixed (benzene and mixed acid) enter the nitrator at the bottom through the pipes shown. These rise in the narrow space between *a a* and *b b*, where they are thoroughly mixed together and finally, when the reaction is finished, flow out continuously at 5. The nitrator 1 can be fitted with a cooling or heating jacket, and water or steam can also be led into 2. 1 can also be fitted with separate circular jackets so that different parts of the pan can be kept at different temperatures. The liquid can also be introduced into 1 at any other point, as shown in the figure. Further, 2 can be fixed and 1 made to rotate, in which case the liquids are introduced into 2. Also several nitrators can be arranged in

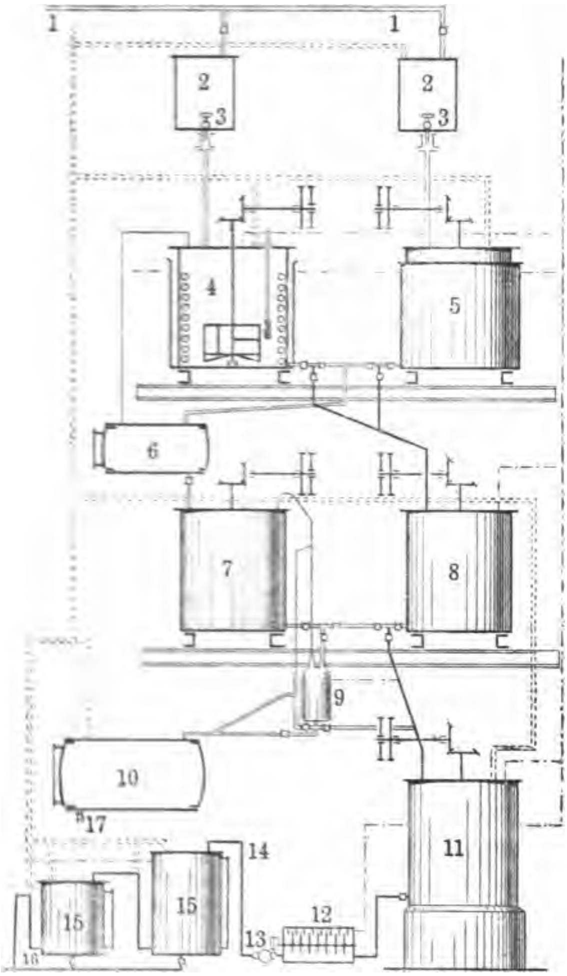


FIG. 8.

1, Pipe supplying mixed acid; 2, acid tanks with taps; 3, opening into a funnel pipe; 4 and 5, nitrators fitted with cooling jackets, cooling coils, thermometers, stirrers, etc.; 6, tank for the waste acid which is run to the denitrator 7, the nitrobenzene running into the washer 8; 8, lead-lined washer for nitrobenzene; 9, separator for the residue of acid from the nitrobenzene; 10, reservoir for mixed acids; 11, tank for washing nitrobenzene with sodium hydroxide; 12, horizontal vessel for washing nitrobenzene with water; 13, pump to transfer nitrobenzene and water through the pipe 14, to the separating tanks 15, where the liquids separate; 16, pipe leading to reservoir for crude nitrobenzene; 17, outlet for waste acid.

The tank, 6, holds a charge of waste acid; two charges of waste acid are treated in 7, and two charges of nitrobenzene in 8. Very little water is used for washing the nitrobenzene in 8 and the wash-water is run to 10. If much water is used for washing, it is run away through separators to catch any nitrobenzene. The same precautions are taken with the alkaline waste water from 11. Two separators, 15, for nitrobenzene and water are shown in the figure, but in practice four are preferable.

the system in series so that, if required, the liquids can be cooled in the first and heated in the second, and so on.*

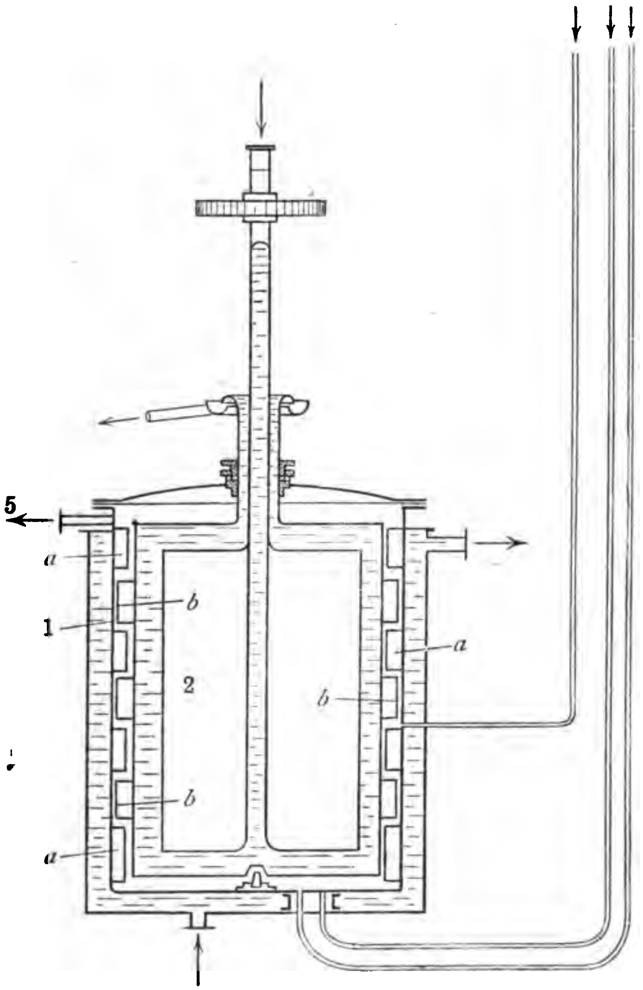


Fig. 9.

The Farbwerke vorm. Meister, Lucius, & Brüning (F.P., 401679; G.P., 201623) describes a plant consisting of four small

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* Another apparatus is described by ter Meer (*Chem. Ind.*, 1914, **37**, 337; Chemische Fabriken vorm. Weiler-ter-Meer, E.P., 16836 of 1910; G.P., 228544), but as this author himself does not recommend it as being an absolutely safe one for the manufacture of nitrobenzene, it is merely noted here.

nitrators fitted with very rapid agitators and connected together in series; the last one is connected to a vertical tower where the nitrobenzene and waste acid separate by gravity and are led off. Benzene and mixed acid are delivered to the first nitrator by means of pumps, which are so regulated as to supply the liquids in the right proportion. The first nitrator is cooled, and the successive ones kept at gradually increasing temperatures so as to deliver the finished nitrobenzene from the fourth.

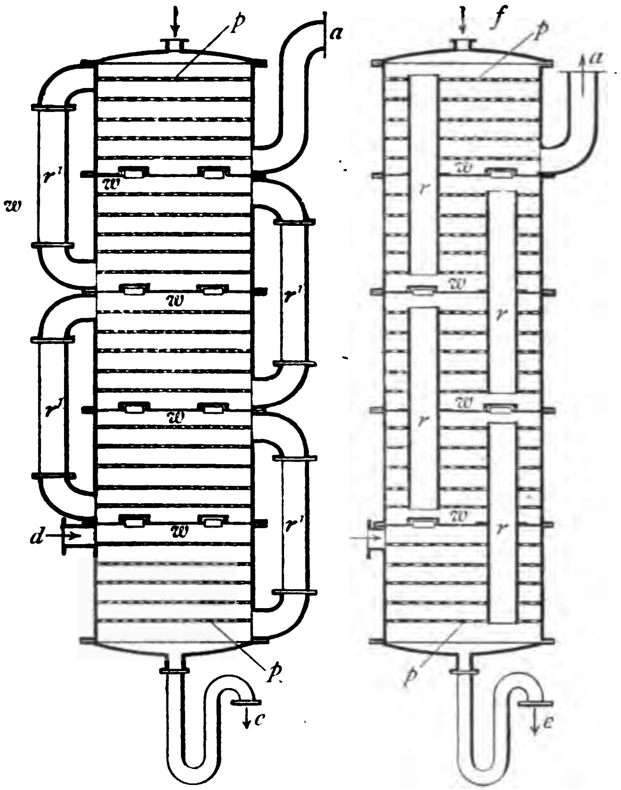


FIG. 10.

Perhaps the most complete and satisfactory plant for continuous nitration is that in which the specially constructed towers or columns of Kubiersky (G.P., 287799) are used. In these the mixed acid enters at the top and the benzene at the bottom. The path of the latter is so arranged (Fig. 10, in which the principle of the towers is shown) that, entering at *d*, it cannot rise past the partitions *w w*, but has to pass downwards through the sieves *p*, and thence to the next higher compartment through *r′* (or *r*), where it again is forced downwards and up into the next higher compartment, and so on. The construction of the tower for the nitration of benzene is illustrated in Fig. 11, and the arrangement of the nitrating plant is shown in Fig. 12.

This consists of three towers, I, II, and III, which are connected together in series so that the reacting liquids can pass from I onwards by gravity. Benzene from the reservoir 1, passing through the measure-tank 11, enters tower I at *a* and fills it up to the overflow and sight-glass 4. The mixed acid from 2 enters the tower at the top (*b*) and falls down the tower in a finely divided condition through the benzene. The waste acid collects at the bottom and is driven into its reservoir, 3, by the liquid pressure, whilst the crude nitrobenzene flows over to tower II. It still contains traces of acid and about 10 per cent. excess of benzene, and is washed in tower II, which is filled with water. The washed nitrobenzene collects at the bottom of this tower and passes through the valve *e* to the distilling tower III. Here the excess of benzene is driven off, by means of steam, which enters the tower at *g*, and is condensed in 5 and 6 and emerges from 9 at *i* (water escaping through *k*), whilst the purified nitrobenzene leaves tower III at *l*, is cooled in the condenser 7, and passes through the sight-glass 8 to 10, where it is separated from the water (escaping through *m*) so that pure nitrobenzene emerges at *n*. The gravity of the crude nitrobenzene

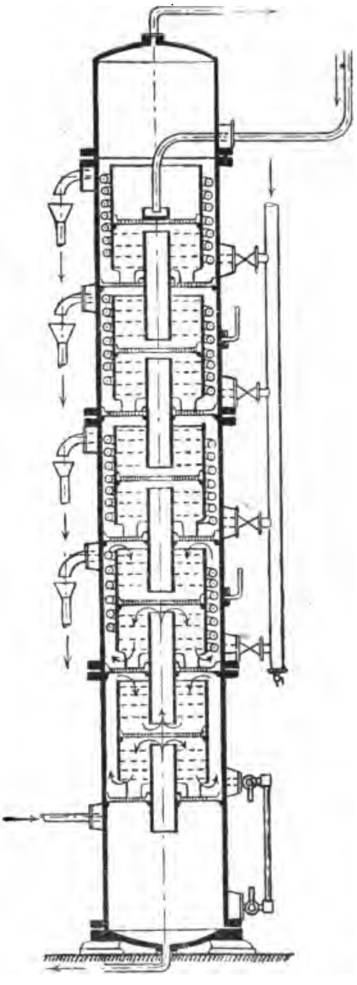


Fig. 11.

is measured at 4 by means of a hydrometer, from the readings of which the flow of benzene and mixed acid is regulated, and thermometers are inserted at various points of the apparatus. As will be seen from Fig. 11, tower I contains four independent cooling coils.

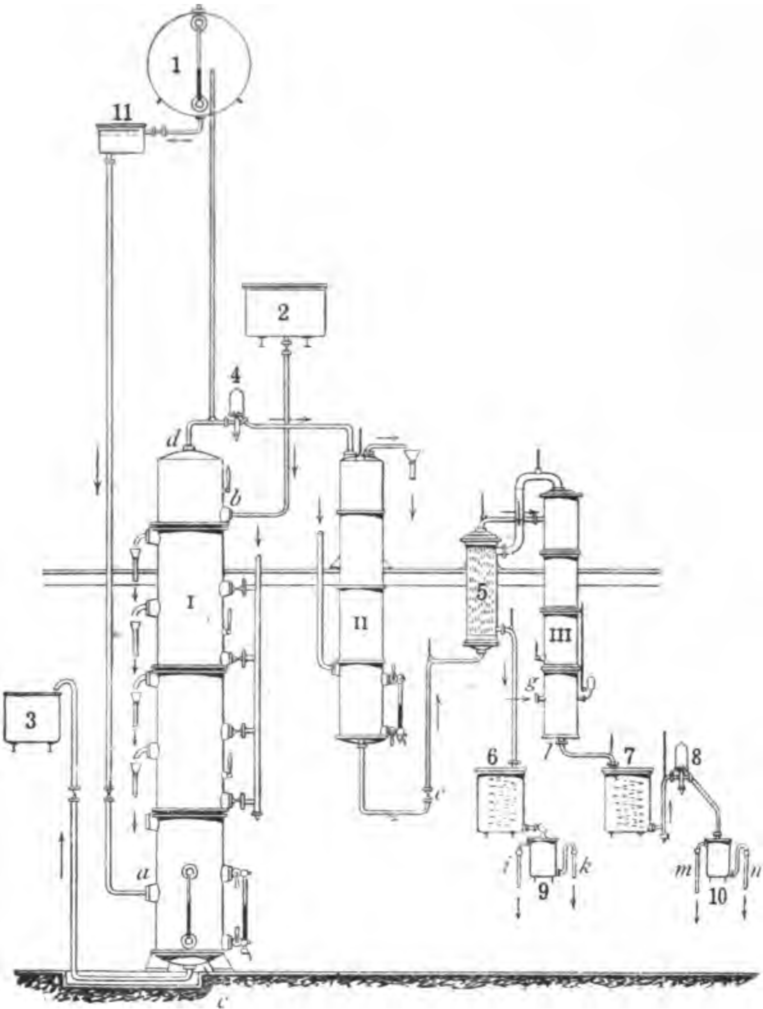


FIG 12.

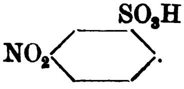
The manufacture of nitrobenzene by using sodium nitrate (the method used originally by Perkin) instead of nitric acid is described by the Saccharinfabrik, A.-G. vorm. Fahlberg, List & Co. (F.P., 401679; G.P., 221787). One hundred and fifty kilos. of sodium nitrate and 35 kilos. of benzene are stirred together in a nitrating pan at 60–80° *; 150 kilos. of 90–96 per cent. sulphuric acid are slowly added, with stirring, when the temperature will rise to about 100°. A further quantity of 65 kilos. of benzene is now added gradually, agitation being continued until the mixture can separate readily into two layers. The sodium hydrogen sulphate is then drawn off and the nitrobenzene worked up in the usual way. The yield is stated to be 150–154 kilos. of washed nitrobenzene, D^{15} 1·18, or 148 kilos. of the pure substance boiling at 96°/18 mm.

Finally, the use of oxides of nitrogen is advocated by the Chemische Fabrik Grünau, Landshoff, & Meyer (G.P., 207170). Nitrogen oxides diluted with air are absorbed by zinc oxide, copper oxide, or similar oxide of low basicity, and the product is heated in an iron tube to 290°, when a mixture of air and benzene vapour is passed through the tube, the temperature being raised. The formation of nitrobenzene begins at 300°, but the temperature must not be allowed to rise above 350°, as otherwise decomposition sets in. The yield, calculated on the nitrogen oxides used, is quantitative.

Nitrobenzene melts at 5·7° (the solidifying point is stated by Friswell, *Trans.*, 1897, 71, 1012, to be 5·0°) and boils at 210·85°/760 mm., or 110°/20 mm. The specific gravity is $D_4^{3\cdot8}$ 1·2220; D_4^{13} 1·2116; D_4^{28} 1·1931 (Friswell). It is fairly readily volatile in steam, 1 part distilling with 6 parts of water under the ordinary pressure.

It is used for the preparation of *m*-dinitrobenzene, aniline, benzidine, metanilic acid, *p*-aminophenol (by electrolysis), quinoline, Induline, Nigrosine, and Magenta.

m-NITROBENZENESULPHONIC ACID,



See under Metanilic acid, p. 47.

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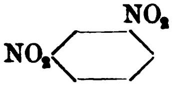
* Care should be taken that the benzene does not disappear by volatilisation. Pikos (*Chem. Zeit.*, 1914, 38, 626) records that in adding 880 kilos. of benzene to a mixture of 920 kilos. of sodium nitrate and 1,200 kilos of sulphuric acid the benzene had been run in too rapidly and had partly volatilised, di- and tri-nitrobenzenes being probably formed. On adding water and warming, an explosion took place on attempting to blow out the contents.

m-DINITROBENZENE,

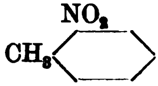


By the nitration of nitrobenzene to dinitrobenzene the chief product is the *m*-dinitro-compound. At 0°, Holleman found (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **2**, 478; compare also Holleman and de Bruyn, *Rec. trav. chim.*, 1900, **19**, 79) that 100 parts of the product consisted of 6·4 per cent. of *o*-, 93·5 per cent. of *m*-, and 0·1 per cent. of *p*-dinitrobenzene.

The process of manufacture and plant required are fully described under Dinitrotoluene (p. 34). As in that case, it is best to nitrate in two stages, the waste acid from the dinitration being fortified with fresh nitric acid and used for the mononitration. For 400 lb. of benzene, a mixture of 480 lb. of nitric acid (75 per cent.) and 720 lb. of sulphuric acid is used for the mononitration, and a mixture of the same amount of nitric acid with 1,350 lb. of sulphuric acid for the dinitration. As in the case of dinitrotoluene, these quantities can be diminished gradually after the process is working satisfactorily.

m-Dinitrobenzene melts at 91° (the technical product at 85–87°), boils at 297° (302·8°/770·5 mm.), and has D^{18} 1·575. It is volatile with steam and is used for the manufacture of *m*-nitroaniline and *m*-phenylenediamine.

o- and *p*-NITROTOLUENE,



and

The nitration of toluene is carried out in the same way as in the case of benzene. For 100 parts of toluene a mixture of 100 parts of nitric acid (75 per cent.) and 150 parts of sulphuric acid is used, and the nitration is carried on at 20–30°. The yield is about 142 parts of nitrotoluene from 100 parts of toluene and the process is fully described under Dinitrotoluene (p. 34).

Another method that has been patented consists in absorbing nitrogen oxides, diluted with air, by zinc or copper oxide which is heated in an iron tube at 290°, and passing a mixture of air and toluene over this. The temperature is gradually increased to 300–350°, and a mixture consisting of about 11 per cent. of *m*- and about 89 per cent. of *o*-nitrotoluene is stated to be obtained (Chemische Fabrik Grünau, Landshoff, & Meyer, G.P., 207170).

The mixture obtained by the ordinary method of nitrating toluene contains about 35 per cent. of *p*-, 63 per cent. of *o*-, and 2 per cent. of *m*-nitrotoluene. (Harmsen, "Die Fabrikation der Theerfarbstoffe," 1889). Fischer (*Zeitsch. Elektrochem.*, 1910, **16**, 161) gives 38, 60, and 2 per cent. respectively.

Friswell (*Proc.*, 1897, **13**, 145) has recorded that variations in the temperature, nitrating mixture, etc., have failed to alter the proportion of about 65 parts of *o*- to about 35 parts of *p*-nitrotoluene.

Holleman (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, **11**, 248 ; *Rec. trav. chim.*, 1909, **28**, 408) nitrated toluene (75 grams) with nitric acid (200 c.c. ; D 1·475) at various temperatures and obtained the following results :—

Temperature.	Ortho.	Meta.	Para.
−30°	55·6	2·7	41·7
0	56·0	3·1	40·9
30	56·9	3·2	39·9
60	57·5	4·0	38·5

The separation of *o*- and *p*-nitrotoluene, after the crude mixture has been well washed, is effected by fractional distillation in a vacuum with the use of a column. Forty per cent. of the mixture is distilled off and consists chiefly of *o*-nitrotoluene, which is redistilled. The residue, on cooling to 0–10°, deposits pure *p*-nitrotoluene. The *o*-nitrotoluene may also be purified by freezing at −5° to −10° until about half the quantity has crystallised. The crystals are centrifuged in a room at −4° and the mother liquor is again frozen (Farbwerke vorm. Meister, Lucius, & Brüning, F.P., 350200 ; G.P., 158219).

On freezing the crude mixture of *o*- and *p*-nitrotoluene to —17° the solid *p*-nitro-compound separates out (Mills, *Phil. Mag.*, 1876, [iv], **1**, 17), and this observation is confirmed by Fischer's work (*loc. cit.*).

o-Nitrotoluene exists in two modifications. The labile or α-form melts at —10·56° and the stable or β-form at —4·14°. (Ostromisslenski, *Zeitsch. physikal. Chem.*, 1906, **57**, 341 ; Knoevenagel, *Ber.*, 1907, **40**, 508, gives — 9·4° and — 3·6° respectively.) It boils at 222·3° and has D^{15} 1·168. When distilled in steam 30 grams pass over with 1 kilo. of steam.

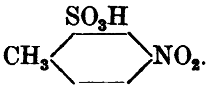
It is used for making *o*-toluidine, tolidine, *o*-nitrobenzyl chloride, and *o*-nitrobenzaldehyde.

m-Nitrotoluene melts at 16·1° and boils at 230–231° ; it has the same density as the ortho-compound.

p-Nitrotoluene melts at 51·4°, boils at 238°, and has D 1·123. When distilled in steam, 20 grams pass over with 1 kilo. of steam.

It is used for making *p*-toluidine, *p*-nitrotoluenesulphonic acid, and *p*-nitrobenzaldehyde.

p-NITROTOLUENESULPHONIC ACID,



p-Nitrotoluene is added to 3 parts of fuming sulphuric acid (containing 23 per cent. of sulphur trioxide) and stirred at 25–30° until a sample is soluble in water. The mixture is poured into 15 parts of saturated salt solution, when the sodium salt of *p*-nitrotoluenesulphonic acid separates almost completely. On cooling, it is filtered off, stirred with saturated salt solution, and filtered again.

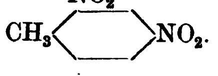
Kastle (*Amer. Chem. J.*, 1910, **44**, 484) obtained the free acid by heating 50 grams of *p*-nitrotoluene with 200 grams of fuming sulphuric acid on the water-bath and pouring the product into 300 c.c. of water, when, on cooling, a thick mass of crystals separated, and van Dorssen (*Rec. trav. chim.*, 1910, **29**, 371) obtained a similar result with 3 parts of fuming sulphuric acid (containing 25 per cent. of sulphur trioxide) under the same conditions of temperature.

The kinetics of the sulphonation of *p*-nitrotoluene have been studied by Martinsen (*Zeitsch. physikal. Chem.*, 1908, **62**, 713).

The acid crystallises from water in pale yellow prisms containing $2H_2O$ (Kastle, *loc. cit.*). The sodium salt is sparingly soluble in water.

It is used for making dinitro- and diamino-stilbenedisulphonic acids and for " Stilbene " dyes, such as Direct yellow RT (Direct yellow F, Naphthamine yellow), Stilbene yellow, Stilbene orange 4R (Chloramine orange G), Polychromine, Diphenylchrysoin G, Chicago orange, Curcuphenine and Chlorophenine orange.

m-DINITROTOLUENE,



The following process is stated to have been carried out in an important English works (Kayser, *Zeitsch. Farb. Ind.*, 1903, **2**, 16, 31). The plant required is as follows :—

(*a*) *Nitrator.*—This consists of a cast iron vertical cylinder about 6 feet high, 4 feet in diameter, having walls half an inch thick and provided with a cover. The cylinder stands in a rectangular wooden box, 4 feet high and about 6 feet square. A nozzle cast on the bottom of the cylinder passes through the front of the box and is made water-tight with gypsum. A short length of iron pipe (about 1½ inches) is screwed into the nozzle, the other end carrying an earthenware or iron tap. The box, provided with a water supply, rests on brickwork some feet from the ground.

The cylinder cover contains two manholes and a small outlet for the escaping gases. A spindle passes through a stuffing-box in the centre. The spindle rests in a removable footstep and carries three parallel agitators, each of which consists of two inclined screw blades. The upper end of the spindle carries a toothed wheel, engaging with one on the shaft which drives the stirring apparatus of several nitrators. The temperature is taken by means of an ordinary laboratory thermometer supported in an iron tube screwed into the nozzle close to the cylinder. The thermometer passes through a rubber cork and is kept in position by means of a screw-cap.

(*b*) *Acid Mixer.*—This is a rectangular cast iron tank, half an inch thick and 5 feet long by 3½ feet wide by 2 feet deep, fitted with a loose overhanging cover in which is a large hole for charging and mixing, and two smaller ones for the escaping air and gases. A thick-walled nozzle is cast on the wide side, into which a cast iron tap, provided with a long handle, is screwed. The acid runs from this into a glass funnel resting in a right-angled piece of inch piping inserted in the side of the nitrating vessel, where it is bent slightly downwards. The acid is mixed in the tank by means of a long iron rod terminating in a disk.

(*c*) *Waste Acid Tank.*—This consists of a lead-lined wooden tank, 7 feet long, 4 feet wide, and 4 feet deep. It stands at a lower level than the nitrators, the acid running from several of these into a lead-lined wooden gutter, and is emptied through an earthenware tap inserted near the bottom.

(*d*) *Boiling-up Tank.*—A similar lead-lined wooden tank, about 7 feet long, 4 feet wide, and 2½ feet deep, somewhat inclined and provided with a tap. A leaden pipe with lateral perforations, resting on bricks, serves for boiling up.

(*e*) *Crystallising Vessels.*—Ordinary glazed earthenware pots, of the shape of a truncated cone, holding about 20 litres.

(*f*) *Drainage Plant.*—This consists of several inclined wide lead-lined wooden gutters or troughs, divided by means of laths, so that each division supports and holds in position a crystallising vessel on its side. Underneath the trough is a system of steam pipes for warming the apparatus.

With regard to the size and arrangement of the plant, several nitrators are necessary, but the tanks described are sufficient for working 1,200–1,600 lb. of toluene or benzene at one operation. If compressed air is available the acid may be mixed in a cast iron vessel in the ground and then blown to *b*.

Method of Working.—Towards the end of the day 700 lb. of sulphuric acid (95 per cent.) are poured into *b*, followed by 450 lb. of nitric acid (75 per cent.). After well stirring, the hole in the cover is closed and the acid allowed to stand. At the same time 400 lb. of toluene, weighed off in screw-capped iron tins, each containing 100 lb. and provided with handles, are tipped into the nitrator. At 7 o'clock the next morning the cooling jacket is filled with cold water, the agitator is started, and acid is allowed to flow in, so that the operation is completed by about 3 p.m., the temperature rising in about one hour to 60° and remaining at that. A better cooling effect can be obtained by corrugating the walls of the nitrating vessels. The agitation is maintained until 5 p.m., when the apparatus is left until the next morning. At 7 a.m., the dark acid is drawn off into carboys until a change in colour denotes the presence of nitrotoluene. The tap is then closed, the agitator started, and the acid prepared the previous day is run in. This consists of 1,350 lb. of sulphuric acid (95 per cent.) and 450 lb. of nitric acid (78 per cent.). The acid is allowed to run in so that by 1 p.m. the operation is complete, the agitation being continued until about 4 p.m. The normal working temperature, which is reached in about 1½ hours, is 115°.

The cooling tank contains no water, and the temperature is regulated by the rate of flow of the acid. Only very little fume is given off. When a sample drawn from the cock solidifies on cooling, the operation is complete. The agitator is then stopped, and after half an hour the spent acid is run into *c* and the oil subsequently into *d*, which is partly filled with boiling water. The boiling is continued for some time, the longer the better, the mixture being stirred with a wooden rod. After then standing for 15 minutes, the oily nitro-product sinks to the bottom, and is drawn off into the crystallising vessels, of which about twelve are filled. The product solidifies in one to two days, according to the time of the year. In the event of a badly conducted operation giving an oily product, the pots are placed on their sides on *f* and slightly warmed, in winter, until oil no longer drips from them. The solid product is eventually turned out of the crystallising vessels and broken up by hand.

After the first operation, it is possible to use the dinitro-waste acid for the manufacture of nitrotoluene. The mixture then consists of only 300 lb. of nitric acid (75 per cent.) with the whole of the waste acid from the dinitro-charge. If fresh acid be used for each charge, it is only necessary to employ for each 400 lb. of toluene 600 lb. of sulphuric acid and 400 lb. of nitric acid, that is to say, the quantities used for the first nitration (mononitrotoluene) can be diminished to these when it is seen that the mononitration is running successfully.

In the manufacture of *m*-dinitrobenzene, the quantities required for the mononitration are: 400 lb. of benzene, 480 lb. of nitric acid (75 per cent.), and 720 lb. of sulphuric acid at a temperature of 70°.

The yield of dinitrotoluene obtained from 400 lb. of toluene, including a small quantity which forms as a crust on the top of the waste acid when cold, is from 700 to 720 lb., equivalent to 90–93 per cent. of the theoretical amount.

The disposal of the waste acid from the nitrotoluene manufacture is an important item in the cost of manufacture. The dark acid, amounting to 13–14 carboys from each operation, has a specific gravity of 133–134° Tw. It can be employed for neutralising the soap lyes from cloth manufacture or for making ferrous sulphate. Employed in the manufacture of nitric acid, it yields at most a nitric acid of 72° Tw. and attacks the retorts to a considerable extent. This is avoided by mixing it with an equal weight of fresh sulphuric acid, when a nitric acid of 88° Tw. (75 per cent.) can be obtained. The acid can also be concentrated in large cast iron pans to 167° Tw., when small quantities of nitrotoluene and nitric acid and much sulphurous acid are given off. The dark product obtained gives a bright nitric acid of 101° Tw.

Analytical Control.—The mononitro-waste acid at 15° should be 132–134° Tw. and contain 1–1½ per cent. of nitric acid by weight (1 c.c. with 10 c.c. of sulphuric acid in a nitrometer giving 6–9 c.c. of nitric oxide). The nitrotoluene, on fractional distillation, should not give more than 1 per cent. of unaltered toluene. A normal dinitro-waste acid should be 150–154° Tw. and contain 3–4 per cent. of nitric acid (1 c.c. giving 20–25 c.c. of gas).

The influence of the composition of the nitrating acid in the direct nitration of toluene to the dinitro-derivative is shown in the following table (Giua, *Gazzetta*, 1915, **45**, II, 32). The liquid product was separated from the solid by draining in a thermostat at 35–40°. The yield of solid product includes that dissolved by the nitrating acid and recovered by diluting with water; the melting point is that of the crude solid product.

Composition of nitrating acid. Per cent.	Weight of toluene. Grams.	Ratio of toluene. to acid.	Solid product.		Yield of liquid product. Grams.
			Yield. Grams.	M.p.	
15HNO_3 78H_2SO_4 7H_2O	40	1 : 10	46	62·5°	30
	40	1 : 15	56·5	50	18
20HNO_3 75H_2SO_4 5H_2O	40	1 : 10	45	65	30
	40	1 : 15	70	54	7
20HNO_3 65H_2SO_4 15H_2O	40	1 : 10	72	56·5	5
	40	1 : 15	64	61	10
25HNO_3 60H_2SO_4 15H_2O	50	1 : 9	74	63	20
	50	1 : 11	69	63	20
30HNO_3 65H_2SO_4 5H_2O	50	1 : 7	68	62	15
	50	1 : 9	63	59·5	22
30HNO_3 55H_2SO_4 15H_2O	50	1 : 9	89	60	7
20HNO_3 60H_2SO_4 20H_2O	50	1 : 10	77	62	15
	500	1 : 10	745	65·7	200

m-Dinitrotoluene melts at 71°, and is used for making *m*-tolylenediamine.

NITROXYLENES.

Commercial xylene is a mixture of *o*-, *m*-, and *p*-xylene, and it contains also a little ethylbenzene.

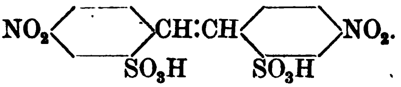
It is nitrated in the same way as benzene or toluene (see pp. 20, 32). For example, a mixture of 90 parts of nitric acid (D 1·4) and 150 parts of sulphuric acid is run into 100 parts of xylene, the temperature being kept below 17° until most of the acid has run in.

The six possible nitroxylenes are all known and five of these are produced in the nitration of xylene; their properties are given in the following table:—

Constitution,					Specific gravity.
CH_3	CH_3	NO_2	M.p.	B. p.	
1	2	3	15°	240°/760 mm., 139°/29 mm.	—
1	2	4	30	254°/748 mm., 143°/21 mm.	1·139 at 30°
1	3	2	13	225°/774 mm.	1·112 at 15°
1	3	4	2	237–239°	1·135 at 15°
1	4	2	liquid	238·5–239°/739 mm.	1·132 at 15°

These nitroxylenes are not separated, but the mixture is reduced and then the various xylidines are isolated.

DINITROSTILBENEDISULPHONIC ACID,



According to Green and Wahl (*Ber.*, 1897, **30**, 3100), 100 grams of sodium *p*-nitrotoluenesulphonate are dissolved in 2 litres of warm water, 200 c.c. of 30 per cent. sodium hydroxide solution and 500 c.c. of a solution of sodium hypochlorite (containing 7 per cent. of active chlorine) are added, and the mixture is warmed at 50° until the sodium hypochlorite has disappeared. On cooling, sodium dinitrostilbenedisulphonate crystallises out. If the product still contains dinitrodibenzylsulphonic acid, it is again oxidised with sodium hypochlorite in sodium hydroxide solution. In the corresponding English Patent (Green, Wahl, and The Clayton Aniline Co., Ltd., E.P., 5351 of 1897), the same process is described, except that 100 lb. of sodium *p*-nitrotoluenesulphonate are employed and the temperature is given as 40°. In the German Patent (*idem*, G.P., 113514) 200 grams of the sodium salt are dissolved in 2 litres of water at 80°, 100 c.c. of 30 per cent. sodium hydroxide solution are added, and immediately 234 c.c. of sodium hypochlorite solution (containing 14 per cent. of active chlorine) are run in until only a slight excess of free chlorine is present. Hydrochloric acid is then added until the solution is only slightly alkaline and the sodium dinitrostilbenedisulphonate separates on the addition of salt.

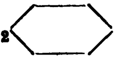
The free acid is obtained by adding excess of hydrochloric acid to a solution of the sodium salt in hot water. It crystallises, on cooling, in colourless or pale yellow needles.

The acid is readily soluble in cold water. The alkali salts are readily soluble in hot, moderately so in cold water, but almost insoluble in water containing sodium hydroxide or chloride. The sodium salt dissolves in 25·5 parts of water at 18°.

Dinitrostilbenedisulphonic acid is used for making the corresponding diamino-acid and for Stilbene yellows, Chloramine orange G (Stilbene orange 4R), Diphenylcitronine G, and Diphenyl fast yellow

Amino-compounds and their Derivatives.

Aniline, NH_2



The usual arrangement now employed (*Chem. Trade J.*, 1906, **38**, 59) is as follows :—

The reduction pan 1 (Fig. 13) is of cast iron, one and three-eighths of an inch thick, with driving gear, agitating shaft, and blades as shown. The pan is fitted with renewable cast iron lining plates at the sides and bottom which protect the machine from the friction caused by the revolving mass of iron borings. The reduction pan is 6 feet 6 inches deep and 4 feet 6 inches in diameter, the total capacity being 650 gallons. Steam is admitted through the vertical shaft, which is hollow, and passes through the extremities of the horizontal revolving blades. Four of these reduction pans, as shown, are required for a production of one ton of aniline oil per day.

If electricity is available, an electrically driven carrier may be fixed to travel over each reduction pan, and this carries an electro-magnet so controlled that it may pick up a suitable quantity of iron borings at one end of the platform, run along to the reduction pan, and, on the current being shut off, drop the borings into the feed hopper, 6. This is a useful arrangement for saving labour.

A charge of 1,000 lb. of nitrobenzene * is run into the receiving pan 12, above the machine. To start the reaction, 1 cwt. of clean cast iron borings, which have been ground by means of an edge runner, 10 gallons of hydrochloric acid, and 6 gallons of water are run in through the funnel-shaped hopper, and simultaneously steam is turned on and the nitrobenzene run in a thin stream into the dish on the top of the machine. The wooden plug in the hopper is driven in tight and the space between it and the hopper is kept full of iron borings. By manipulating the plug, the borings can be added without allowing any vapour to escape. Distillation proceeds, and the distillate passes through the condenser and runs back into the dish, together with the nitrobenzene which is carried over. The iron borings and nitrobenzene are added only in sufficient quantity to maintain a constant level in the dish. If the reaction proceeds too violently, loss is caused by the formation of benzene. When the level of the liquid in the dish begins to lower, the supply of nitrobenzene and iron

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* In some works, large reducing pans are used in which 3 tons of nitrobenzene can be reduced in one charge.

borings is increased. The process is continued until the whole charge of nitrobenzene is run in, which takes about ten hours. The total weight of iron borings required is 9 cwt. A sample

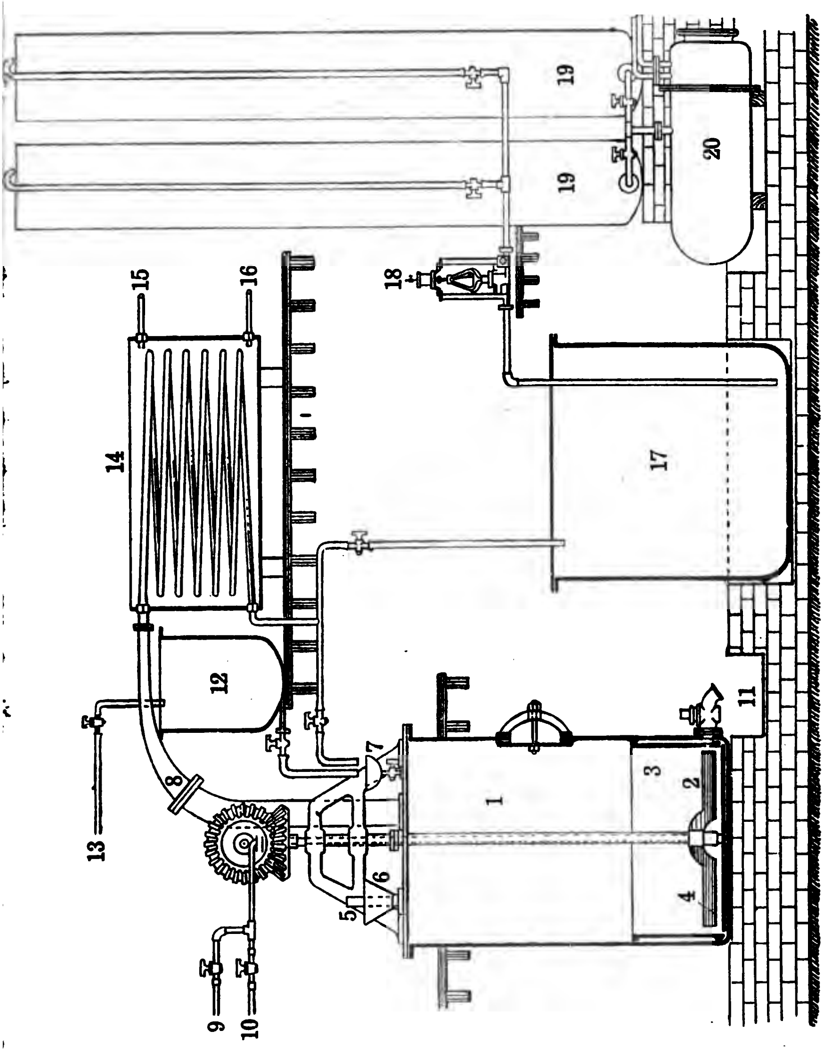

FIG. 13.—ANILINE OIL PLANT.—1. Aniline pan; 2, agitating blades; 3, side lining plates; 4, bottom lining plates; 5, wood plug for hopper; 6, feed hopper for borings; 7, charging dish; 8, vapour pipe to condenser; 9, pure steam pipe; 10, aniline steam pipe; 11, gutter; 12, receiving pan; 13, pipe from nitrobenzene tank; 14, condenser; 15, overflow; 16, cold water inlet; 17, receiver; 18, steam pump; 19, settling tanks; 20, air-pressure egg.

caught as it runs from the condenser should then be quite free from nitrobenzene, and the reduction pan will contain only aniline oil, water, and oxide of iron. The supply of steam is then increased, so as to distil over the aniline oil* and water, and the distillate is diverted into the tank 17. The steam used for this distillation is not pure steam, but is generated from the aniline water mentioned below in a separate boiler as shown in the plan. The aniline water is that which separates from the oil in the separating tanks 19, and contains about 2 per cent. of aniline oil in solution. The aniline and water in the tank 17 are pumped into the settling tanks 19 and allowed to settle for twenty-four hours. The distillation of the oil and water from

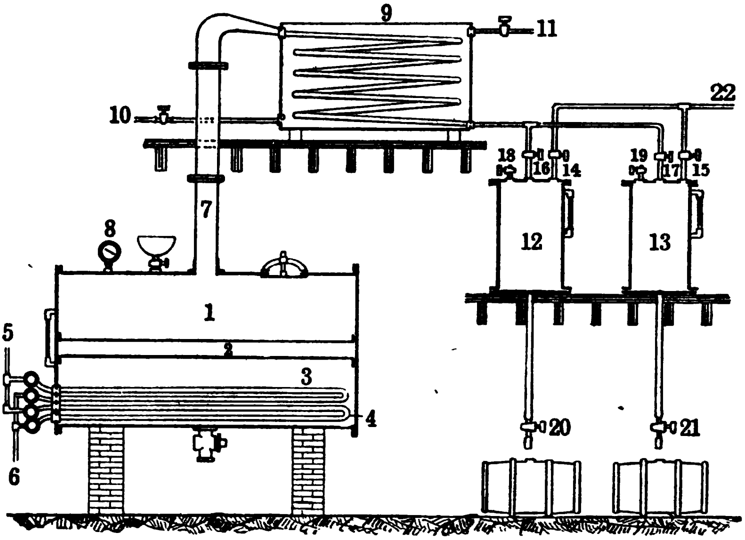

FIG. 14.—VACUUM STILL FOR ANILINE OIL.

1. Vacuum still.
2. Internal hollow stay.
3. Steam tubes.
4. „ „
5. Steam inlet.
6. „ outlet
7. Vapour pipe to condenser.
8. Pressure gauge.
9. Condenser.
10. Cold water inlet.
11. Overflow for water.
12. Receiver for distilled oil.
13. „ „ „
14. Connexion from vacuum pump.
15. „ „ „
16. Inlet from condenser.
17. „ „
18. Air admission tap.
19. „ „
20. Run-off tap for distilled oil.
21. „ „ „
22. Connexion from vacuum pump.

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* In some works, the aniline is allowed to settle, drawn off, settled from dirt, and then distilled, the liquid remaining in the reduction pan being treated with steam as above. In others, the contents of the pan are run through a filter-press and allowed to settle.

the machines takes about seven hours, and during the last hour pure steam is again used, so that when the operation is finished the condensed water left in the machine will be free from aniline, and can be used for flushing out the oxide of iron into the gutter which runs to settling tanks or simply settling beds in the ground outside the building. The aniline oil which has settled to the bottom of the settling tanks is run into the egg below and blown into the vacuum still or into a store tank, where it is stored until rectification is proceeded with. The aniline water left in the settling tanks 19 is blown to the water tank feeding the aniline water boiler.

The final purification of the crude aniline oil is done in a vacuum still (Fig. 14). The body of the still is wrought iron, 15 feet long and 7 feet 6 inches in diameter, having a total capacity of 4,000 gallons. A smaller still may be used, but it is best to distil as much as possible in one operation. The steam is supplied from a boiler having a working pressure of 100 lb. per sq. inch, at which pressure the steam has a temperature of 170°. The internal steam tubes are wrought iron, 2 inches in diameter.

Bent tubes are employed which enter and return to the same end of the still. The column 7 is of cast iron, 18 feet high and 9 inches in diameter. The condensing coils consist of three flat copper coils, 2 inches in diameter, arranged side by side in a wrought iron tank, the distillate entering all the three coils simultaneously from the still-head by means of branch pipes. The total length of copper pipe in the condenser is 432 feet. The two receivers permit continuous working, so that when the first is full, as indicated by the gauge-glass tube, it is shut off and the second brought into use. The contents of the first can then be drawn off while the second is being filled, and the vacuum is thus maintained throughout.

The still is charged with 35,000 lb. of crude aniline oil and steam is turned on. The first fraction, about 7 per cent. of the distillate, consists of aniline and water, which is added to the crude oil and water in the settling tanks 19. The next fraction is "light aniline," and consists of aniline oil with a small quantity of benzene. If the reduction of the nitrobenzene has been carefully performed, this fraction is only about 4 per cent. of the distillate. It is collected and redistilled, giving pure aniline and benzene, the latter being returned to the nitrobenzene department to be nitrated. The next fraction is pure aniline oil, clear and water-white. The tail end, called "last runnings," forms about 5 per cent. of the distillate, and, on redistillation, yields 80 per cent. of pure aniline. The total yield of pure aniline obtained from nitrobenzene is 71¾ per cent. As the pure benzene yields 154½ per cent. of nitrobenzene and the latter 71¾ per cent. of aniline, the total yield of pure aniline from pure benzene is 110·85 per cent. Compared with theory, there is little room for improvement.

In America, reducing pans of a capacity of 1,000 gallons are used (*Cotton*, 1916, **80**, 578; compare also Stevens, U.S.P., 1267819) and the yield is stated to be 116 parts of aniline from 100 parts of benzene. A plant for turning out 1,000 lb. of aniline per day would require a building 75 feet long, about 30 feet wide, and about 25 feet high, approximately 10 horse-power to drive the necessary pieces of moving machinery and about 500 lb. of steam per hour, or 15 boiler horse-power.

Other processes which have been proposed for the manufacture of aniline may be briefly noted:

Reduction of Nitrobenzene with Sodium Disulphide.—Kunz (G.P., 144809) prepares sodium disulphide, Na_2S_2, by dissolving sulphur in a boiling solution of sodium sulphide, and nitrobenzene is readily reduced to aniline by boiling with this solution. The sodium thiosulphate which is formed is recovered, after distilling off the aniline, by evaporation and crystallisation.

Catalytic Reduction of Nitrobenzene.—I. *With Copper.*—According to Senderens, d'Andoque de Sériége, and de Chefdebien (F.P., 312615; G.P., 139457), water-gas is passed over finely-divided black copper oxide at 300–400°, whereby the oxide is reduced. Nitrobenzene vapours are then led over this and are reduced to aniline. The patent claims the use of copper, nickel, cobalt, iron, and platinum.

The Badische Anilin- & Soda-Fabrik (E.P., 13149 and 15334 of 1914; 5692 and 6409 of 1915; G.P., 282568; U.S.P., 1207802) prepares the contact mass as follows: Hot sodium hydroxide solution is added gradually to a solution of 1,180 grams of copper nitrate crystals, 38 grams of silver nitrate, and 252 grams of magnesium nitrate crystals, and the precipitate washed; 130 grams of pumice-stone lumps are treated with 20 grams of the precipitate, a small amount of water, and then 20 grams of 40 per cent. sodium silicate solution added, and the pasty mass obtained is heated at 200° in a current of hydrogen; on passing a mixture of hydrogen and nitrobenzene vapour over this catalyst at 200–210°, aniline is produced.

The reduction can also be carried out with a mixture of nitrobenzene vapour with carbon monoxide and steam, there being in the reducing gas at least one volume of water vapour for each three volumes of carbon monoxide. In this case, the catalyst is prepared by coating 130 grams of pumice stone with a mixture of 24·3 grams of cupric carbonate, 2·7 grams of zinc carbonate, and 20 grams of concentrated sodium silicate solution and reducing at a low temperature. During the passage of the nitrobenzene vapour the temperature is maintained at 200–220°. A mixture of hydrogen and carbon monoxide may also be used.

II. *With Nickel.*—Brochet (E.P., 16936 and 22523 of 1913; F.P. 458033 and First addition; U.S.P., 1247629) passes hydrogen into a thoroughly stirred mixture of nitrobenzene and reduced nickel at 100–120°, the pressure being 10–15 kilos. per sq. cm.

The Farbwerke vorm. Meister, Lucius, & Brüning (G.P., 282492) passes a mixture of steam and hydrogen through nitrobenzene at 120°, and the gases then pass through a long tube half filled with finely-divided nickel, and the vapours are condensed. The yield of aniline is almost theoretical.

III. *With Iron Oxides.*—The Chemische Fabrik vorm. Weiler-ter-Meer (F.P., 462006) passes a mixture of hydrogen and nitrobenzene vapour over finely-divided and heated ferrous oxide or magnetic oxide which is mixed with asbestos or kieselguhr. The iron oxides are not reduced during the process.

IV. *With Iron.*—Von Girsewald (G.P., 281100) reduces nitrobenzene by hydrogen or a mixture of hydrogen with carbon dioxide in the presence of water and iron borings, under high pressure and at a temperature above the boiling point of aniline.

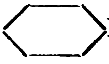
V. *With Silver or Gold.*—Pumice is coated with silver and a mixture of hydrogen and nitrobenzene passed over at 230°. With gold as the catalyst, the temperature is 230–250°. A mixture of gold and silver may be used (Badische Anilin- & Soda-Fabrik, G.P. 263396).

Electrolytic Reduction of Nitrobenzene.—It would appear that experiments on the electrolytic reduction of nitrobenzene have not yet emerged from the experimental stage. Various patentees claim an almost theoretical yield, but the relatively large quantities of additional substances to be mixed with the nitrobenzene in the electrolytic cell (such as hydrochloric acid, salt solution, copper powder, cuprous or ferrous chloride, etc.) would seem to render the process too expensive.

Interaction of Chlorobenzene and Ammonia.—According to the Aktiengesellschaft für Anilinfabrikation (E.P., 3966 of 1908;

F.P., 397485; G.P., 204951) a mixture of chlorobenzene (200 parts), 25 per cent. solution of ammonia (600 parts), and copper sulphate (25 parts) is heated in a closed vessel for about twenty hours at 180°, the temperature being raised to 200° towards the end. The mass is then acidified with sulphuric acid, the aniline sulphate filtered off, and converted into the base in the usual manner. The yield of aniline is about 80 per cent. of the theoretical.

Aniline melts at — 6·2° and boils at 80–81°/20 mm. and 184·4°/760 mm. It has D^{15} 1·026. One hundred parts of a saturated solution in water contain 3·61 parts of aniline at 13·8°, 3·66 parts at 22·7°, 4·3 parts at 52°, and 6·12 parts at 86·6° (Sidgwick, Pickford, and Wilsdon, *Trans.*, 1911, **99**, 1124). It is used for making methyl- and dimethyl-aniline, ethyl- and diethyl-aniline, benzylmethylaniline, benzylethylaniline, quinoline, quinaldine, phenylhydrazine, diphenylamine, acetanilide, formanilide, sulphanilic acid, phenylglycine, aminoazobenzene, Aniline black, Induline, Nigrosine, Magenta, Pararosaniline, Aniline blue, Oil yellows, Chrysoidines, Ponceaus, Scarlets, Orange G, Chromotropes, Fast acid fuchsine B, Amidonaphthol red G, Tolan reds, Brilliant lake red R, Blue black N, Domingo blue blacks, Naphthol blue black, Chrome patent greens, Neutral grey G, Sulphone blacks, Erie direct blacks (Union blacks, Cotton blacks), Erie direct green ET, Columbia black green D, etc.

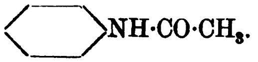
ANILINE HYDROCHLORIDE,  NH_2,HCl.
(ANILINE SALT).

The calculated amounts of aniline and pure hydrochloric acid are mixed in earthenware, lead-lined, or nickel-lined vessels and the mixture allowed to cool. The crystals which separate out are centrifuged and dried at a low temperature on glass or lead trays. The mother liquors can be neutralised with lime and the aniline distilled over in a current of steam, or they may be evaporated and the impure salt used for making Magenta, etc. The preparation of aniline hydrochloride by evaporating the constituents in a vacuum is described by Welter (E.P., 15836 of 1895).

Aniline hydrochloride forms grey crystals melting at 198°, and readily soluble in water or alcohol.

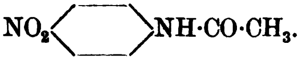
It is used largely for the production of Aniline black, Magenta, etc.

ACETANILIDE,



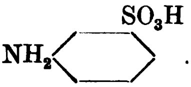
See under *p*-Nitroaniline (p. 51).

p-NITROACETANILIDE,



See under *p*-Nitroaniline (p. 53).

METANILIC ACID,

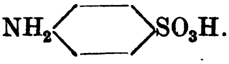


This is prepared by sulphonating nitrobenzene and reducing the resulting nitrobenzenesulphonic acid. The following details are given by Paul (*Zeitsch. angew. Chem.*, 1896, **9**, 686).

Seventy-five kilos. of nitrobenzene are run in a thin stream into 150 kilos. of fuming sulphuric acid, whereby the temperature rises to about 100–105°. After being heated for about two hours at 110–115° the mixture is blown into a tub containing 1,000 litres of water and reduced with 75 kilos. of ground cast iron borings, which are added within 1½–2 hours. The solution is boiled, neutralised with milk of lime, and filtered, the gypsum being washed twice. The filtrate is evaporated to 22–24° Bé., and, after cooling, filtered from the separated calcium sulphate. The yield is 300–320 kilos. of solution (32–36 per cent.) corresponding with 100–110 kilos. of metanilic acid. The solution is used directly for making azo-dyes.

The acid crystallises with half a molecule of water and is used chiefly for making Metanil yellow.

SULPHANILIC ACID,



Sulphanilic acid may be prepared by heating aniline with 2 parts of sulphuric acid to 180–190°, but is usually manufactured by heating aniline acid sulphate, $C_6H_5{\cdot}NH_2$, H_2SO_4, the so-called "baking" process for which Paul (*Zeitsch. angew. Chem.*, 1896, **9**, 685) gives the following recipe.

Twenty-seven kilos. of sulphuric acid (66° Bé.) are placed in a cast iron pan fitted with a stirrer, and 24 kilos. of aniline added in a thin stream, during three to four hours. The stirring is continued for a further three to four hours. The yield of acid sulphate is 49·6–49·7 kilos.

Thirty-two kilos. of the sulphate are placed in a shallow iron rectangular pan resting on an iron support in a cast iron oven fitted with a small chimney so as to allow the hot gases to escape.

The temperature is kept at 230–235° until no more sulphur dioxide escapes. The mass, when cold, is ground in a ball mill. The yield is 29·5–29·6 kilos. of sulphanilic acid. It is dissolved in dilute sodium hydroxide solution, filtered from a little carbonaceous matter, and the solution boiled to expel a little free aniline. The solution is then used directly for making azo-dyes, or the free acid may be obtained by acidifying.

Nevile and Winther (*Ber.*, 1880, **13**, 1940) mix 100 parts of aniline with 105 parts of concentrated sulphuric acid and bake at 180–220°.

Mühlhäuser (*Dingl. Polyt. J.*, 1887, **264**, 181) heated 100 parts of aniline with 105 parts of sulphuric acid for six hours at 220–230° and obtained a yield of 92·5 per cent. of the theoretical.

Another variation is to mix 100 parts of aniline with 115 parts of sulphuric acid and to heat the sulphate up to 205° during four hours and continue heating at this temperature for six hours. The product is dissolved in 4000 parts of one per cent. sodium hydroxide solution and worked up as above.

It is best to spread the sulphate on trays and heat these in an oven by means of superheated steam circulating through pipes, or to bake in a vacuum oven (like a vacuum drier), the trays resting on shelves through which hot gases are led.

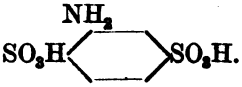
A later process (Aktiengesellschaft für Anilinfabrikation, E.P., 3966 of 1908; F.P., 397485; G.P., 205150) consists in heating *p*-chlorobenzenesulphonic acid with aqueous ammonia and copper chloride at 170° for twelve hours, but the yield is only 80 per cent. and the process would not appear to offer any technical advantage over the one described above.

Sulphanilic acid forms two hydrates. The dihydrate, obtained by crystallisation from its solution below 20°, is very efflorescent and on exposure to the air soon loses all its water. The monohydrate, which separates between 20° and 44°, retains its water at the ordinary temperature. One hundred grams of a saturated solution contain 0·444 gram of anhydrous acid at 0°, 1·093 grams at 18·9°, and 2·85 grams at 54·5°, or, in other words, sulphanilic acid is soluble in 224 parts of water at 0°, 90 parts at 18·9°, and 34 parts at 54·5° (Philip, *Trans.*, 1913, **103**, 284). Except at 0°, the earlier figures given by Doliński (*Ber.*, 1905, **38**, 1835) agree fairly well with the above. This author found that the acid is soluble in 156 parts of water at 0°, 92·5 parts at 20°, 40·9 parts at 50°, and 14·9 parts at 100°.

Sulphanilic acid is used for making Helianthin (Methyl orange, Orange III), Orange I, II and IV, Resorcine yellow, Fast fuchsine

G, Resorcine brown, Acid brown, Buffalo black PY (Palatine black A, Wool black 4B, 6B), Anthracene acid brown, Ponceau 10 RB, Eriochrome verdon A, Buffalo black 10B, Victoria black B, Eboli greens, Benzamine brown, Direct brown GR (Naphthamine brown 4G), Columbia green (Direct green CO), Benzo brown G, and Hessian brown BBN.

Aniline-2 : 5-disulphonic Acid,

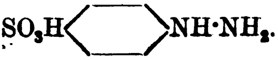


Twenty-six kilos. of sodium 4-chloro-3-nitrobenzenesulphonate (p. 13) are dissolved in 50 litres of water, 30 kilos. of crystallised sodium sulphite are added, and the mixture is boiled under reflux for one to two hours. On cooling, sodium 2-nitrobenzene-1 : 4-disulphonate partly separates and the remainder is salted out.

Thirty-two kilos. of the crude sodium salt are dissolved in 200 litres of water, 10 litres of acetic acid (30 per cent.) are added, and then 30 kilos. of iron powder at the temperature of the water-bath. When the reduction is finished, the liquid is rendered alkaline by the addition of sodium carbonate, filtered and the filtrate evaporated somewhat. On acidifying, the acid sodium salt of aniline-2 : 5-disulphonic acid is precipitated (Badische Anilin- & Soda-Fabrik., G.P., 77192).

The free acid crystallises with $4H_2O$. It is used for making ethyl-*m*-aminophenol.

Phenylhydrazine-*p*-sulphonic Acid,



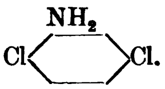
This is prepared either by sulphonating phenylhydrazine (Gallinek and Richter, *Ber.*, 1885, **18**, 3172), obtained by reducing diazotised aniline with sodium hydrogen sulphite (Fischer, *Annalen*, 1878, **190**, 69), with 5–6 parts of sulphuric acid at 100° or by reducing diazotised sulphanilic acid. The latter is the method generally used.

Twenty-three kilos. of sodium sulphanilate and 7 kilos. of sodium nitrite (97 per cent.) are dissolved in 120 litres of water. The solution is cooled by ice and added to a mixture of 17 kilos. of sulphuric acid (66° Bé.) and 100 litres of water, also cooled by ice. The diazotised sulphanilic acid is filtered off and washed with cold water. Great care must be taken that no part of this is allowed to dry, as it is very explosive. The paste is mixed with a little water and added to a solution of 30 kilos. of sodium sulphite in 300 litres of water which has first been saturated with sulphur dioxide, giving a 17 per cent. solution of sodium hydrogen sulphite (22° Bé.). The diazo-compound dissolves with a yellow coloration which soon disappears. Fifty kilos. of concentrated hydrochloric acid are then added and the solution is evaporated to crystallisation. The acid is filtered off, washed, and may be recrystallised from boiling water (*Rev. prod. chim.*, 1917, **20**, 21).

The acid crystallises with $\frac{1}{2}H_2O$ and is sparingly soluble in cold but readily so in hot water. The alkali salts are readily soluble.

It is used for making Tartrazine (Buffalo Yellow) and for pyrazolone derivatives.

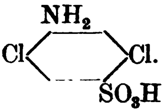
2 : 5-Dichloroaniline,



This is prepared from 2 : 5-dichloronitrobenzene (p. 14) by reduction with iron and a little hydrochloric acid in the same way as aniline is obtained from nitrobenzene.

2 : 5-Dichloroaniline melts at 50° and boils at 246°/744 mm. It is used for making Chloramine black N, Chloramine green, and Chloramine blues.

2 : 5-Dichloroaniline-4-sulphonic Acid,

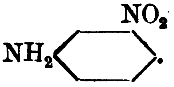


Forty grams of 2 : 5-dichloroaniline are added to 120 grams of cooled, fuming sulphuric acid (containing 18 per cent. of sulphur trioxide) and the mixture is heated at 170–180° for about two hours until all the base has disappeared. It is then poured on ice, when the sulphonic acid separates out. The acid is fairly readily soluble in hot water, and the sodium salt, which crystallises with $5H_2O$, is readily soluble (Noelting and Kopp, *Ber.*, 1905, **38**, 3513).

The acid is also obtained by employing fuming sulphuric acid containing 20–25 per cent. of sulphur trioxide and heating the mixture at 120° (Chemische Fabrik vorm. Sandoz, E.P., 3373 of 1908 ; F.P., 387245 ; G.P., 222405 ; U.S.P., 901675).

It is used for the preparation of 2′ : 5′-dichloro-4′-sulpho-1-phenyl-3-methyl-5-pyrazolone.

m-NITROANILINE,

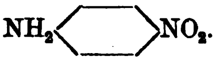


m-Nitroaniline can be obtained by adding aniline nitrate to sulphuric acid at a low temperature (Levinstein, G.P., 30889) or by reducing *m*-dinitrobenzene with iron and sulphuric, hydrochloric, or acetic acid (Anilinölfabrik von A. Wülfing, G.P., 67018), but the best method is to reduce *m*-dinitrobenzene with sodium disulphide (Cobenzl, *Chem. Zeit.*, 1913, **37**, 299). Fifty kilos. of *m*-nitrobenzene and 2,000 litres of water are placed in a tub fitted with a good agitator and the mixture is heated to boiling and well stirred so as to bring the molten dinitrobenzene into a fine state of division. A solution of sodium disulphide, Na_2S_2, prepared by dissolving 20 kilos. of flour of sulphur in 75 kilos. of crystallised sodium sulphide (or 25 kilos. of the anhydrous sulphide) and 300 litres of water, is now added gradually so as to keep the whole boiling, and, after the addition, boiling is continued for some time until a test shows that the reduction is finished. The whole is filtered through a filter press into a tub below it, in which, on cooling, the *m*-nitroaniline crystallises in yellow needles. The excess of sulphur employed (10 kilos.) remains in the filter press and is used in the next reduction. The *m*-nitroaniline is collected, washed, and dried. The yield is about 35 kilos. or 80 per cent. of the theoretical.

m-Nitroaniline melts at 112·4° and boils at 285°. It is soluble in 600 parts of water at 18·5° and readily so in boiling water. It has a specific gravity of 1·43.

It is used for making azo-dyes, particularly Alizarin yellow GG.

p-NITROANILINE,



The manufacture of paranitroaniline is usually carried out by treating a solution of acetanilide in sulphuric acid with a mixture of nitric and sulphuric acids at a low temperature and hydrolysing the product. The following is an account of the manufacture given by Müller (*Chem. Zeit.*, 1912, **36**, 1055). Earlier processes, which are not so satisfactory, are given by Noelting and Collin (*Ber.*, 1884, **17**, 262), Pokorny (*Bull. Soc. Mulhouse*, 1894, **64**, 280), and Walter ("Aus der Praxis der Anilinfarbenfabrikation," 1903). Some purely scientific work on the nitration of aniline and acylanilides, which, however, is of little interest to the manufacturer and is therefore not quoted here, has been carried out by Holleman, Hartogs, and van der Linden (*Ber.*, 1911, **44**, 704) and by Tingle and his co-workers (*Amer. Chem. J.*, 1906, **36**, 605; *J. Amer. Chem. Soc.*, 1908, **30**, 822, 1355, 1587, 1764; 1909, **31**, 1312).

Preparation of Acetanilide.—This is done in an aluminium pan of 1,400 litres capacity (Fig. 15), having walls 1¼ inches thick and surrounded by an iron pan which is bricked in and can be heated to a red heat. The air-space between the two pans is 1½ inches. The aluminium lid, flanged on, carries a dome of aluminium plate in which three funnel-shaped baffles are placed, with an opening of 2 inches in diameter. At the top of the dome is a cork set not too firmly, so as to act as a safety valve. Emerging from the side of the dome are two aluminium pipes with well lubricated aluminium taps which connect with a cooling tube of aluminium or silver. The lid has a manhole for charging, connexion for compressed air, and hole for a glass tube carrying a thermometer. At the end of the operation this tube is taken out and an iron tube inserted and flanged on, through which the batch is blown. The aluminium pan lasts at least ten years, and the dome (walls ½ inch thick) requires renewing after five years. The aniline and acetic acid can be poured directly into

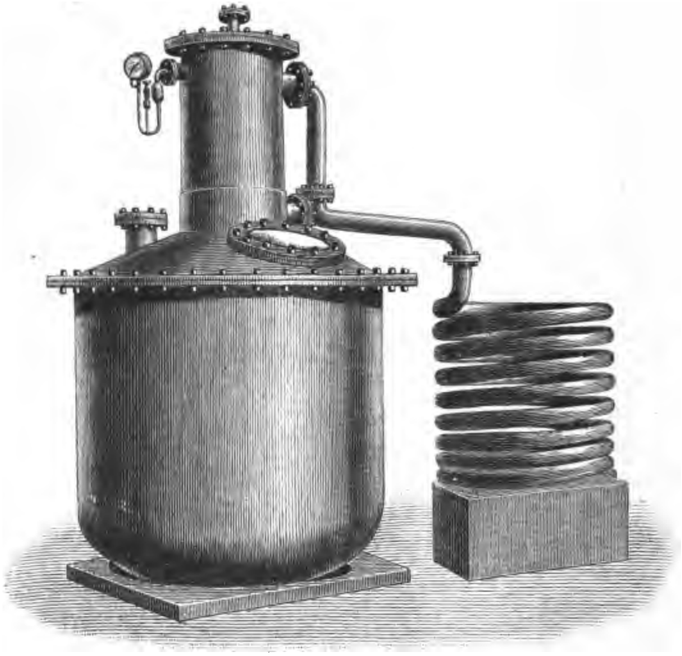


FIG. 15.

the pan through the manhole, but it is convenient to use an aluminium egg (750 litres capacity), with a flanged aluminium lid, from which the aniline and acetic acid are blown to the pan by means of an aluminium pipe and rubber tubing.

The finished batch is blown through the iron tube on flat pans of wrought iron, where it solidifies and is broken up, and ground in a disintegrator.

While the pan is still warm (from a previous batch), first the aniline (750 kilos.) and then the glacial acetic acid (600 kilos.) are filled in. On the first day and first night the iron pan is heated with a small fire so that the thermometer shows 120°. A few lumps of pumice stone are put in to avoid bumping. These may be about the size of one's fist. During the heating, tap II is closed so that the vapours must go up the dome. The vapours distil through tap I and are collected in a carboy. In this time (one day and one night) about 2 carboys (70–75 litres) of dilute acetic acid (14–24 per cent.) distil over. On the second day, early, 150 kilos. of glacial acetic acid are added and the heat is increased so that the thermometer at midday is 150° and at 8 p.m. is 240°. During the second day 4–5 carboys of dilute acid distil over, which gradually becomes stronger. The first carboy contains about 28 per cent. acid, the second 34 per cent., the third 45 per cent., and the rest 70–75 per cent. When the temperature on the evening of the second day reaches 240° the heat is shut off and the pan allowed to cool. Acetic acid will go on distilling for some hours. Next morning the thermometer is 160–180°, and the batch is blown over into the iron pans. Next day it is broken up and ground in a disintegrator. The yield is 1,050–1,070 kilos. of acetanilide melting at 108–110°.

Nitration.—For this is required a cast iron pan fitted with a lid and a very efficient stirrer. This may be of the propeller type, or a spiral stirrer surrounded by a cylinder. The pan may be cooled from outside with ice and salt, but it is much better to fit the pan with cooling coils, from an ice-plant (cold salt solution).

For the undermentioned quantities the capacity of the pan would be about 900 litres.

Two hundred kilos. of powdered acetanilide are added while stirring to 800 kilos. of sulphuric acid (66° Bé.). The temperature rises slowly, but must not exceed 30°. When all is dissolved, the solution is cooled to 0° and a mixture of 152 kilos. of nitric acid (40° Bé.) and 150 kilos. of sulphuric acid (66° Bé.) is slowly run in, the temperature not being allowed to rise above 3°.

When all the acid is in, the batch is stirred for two to three hours longer. A small sample is taken, poured on ice, and the nitroacetanilide filtered and well washed with cold water. The precipitate is hydrolysed in a test-tube with dilute sodium hydroxide solution, whereby a clear yellow solution should result. If the acetanilide has not been completely nitrated, aniline will be detected. In some works a sulphonation pan is used for dissolving the acetanilide and the solution transferred to the nitrating pan. The batch is now blown with compressed air, or run out from the bottom tap if the pan is so fitted, into 2,500 litres of water and 1,200 kilos. of ice. The whole is filtered through a wood filter-press, the cake washed carefully in the press to remove acid, then mixed with 2,500 litres of water, neutralised with 25–26 kilos. of sodium carbonate, and again filtered. The yield of nitroacetanilide is 85–88 per cent. of the theory reckoned on acetanilide. In many works the nitroacetanilide, after being thoroughly washed (until the wash-water is almost neutral), is mixed with water, boiled up, and a few kilos. of sodium carbonate are added until a weak alkaline reaction is obtained. The ortho-compound is thus easily hydrolysed whilst the para- is unchanged. The latter is then filtered a second time and washed, whereby the ortho- passes away in the wash-water. In one works the nitration is run into water at 30°. Using, for example, 300 kilos. of acetanilide, the batch is run into 10,000 litres of water at 30°. It is stirred for an hour, filtered, and washed with cold water. In this case the paste is not mixed up again with water.

The para-nitroacetanilide, when sold as such, is dried at 80–90° and ground.

Hydrolysis.—Usually several nitrations are hydrolysed at once. For example, with a nitration in which 300 kilos. of acetanilide have been used, the washed press-cake from three batches (if 200 kilos. of acetanilide had been taken, this would be four and a half batches) is placed in a large tub with stirrer, in which 1,000 litres of water and 550–700 kilos. of 35 per cent. sodium hydroxide solution are contained. The whole is heated to boiling and kept at this point for two to three hours. The vapours are very poisonous, so that the tub must be covered and connected by means of a wooden passage to a flue. A little more than the theoretical amount of sodium hydroxide is taken. The solution during hydrolysis must always be weakly alkaline. The hydrolysis is finished when a sample dissolves clear in hydrochloric acid. The whole forms a yellow solution in which yellow crystals of *p*-nitroaniline are suspended. It is now run into a large tub, in which wooden taps are fitted in the side, allowed to settle for half an hour, and the mother liquor drawn off through the wooden taps and collected in a large tank. The tub is filled up with fresh water to the former volume, and the batch boiled up, care being taken that a faint alkaline reaction is present. After 30–45 minutes' boiling the batch is allowed to settle and the liquor drawn off. This is also collected. Then, in a separate tub, the batch is allowed to cool until the next day and thrown on a vacuum filter or passed through a filter-press, washed with a little cold water, and dried on wooden trays at 80°. Care must be taken in handling the dry product, as it is very toxic and produces aniline poisoning. The *p*-nitroaniline is then very carefully ground in ball mills, which generally takes twenty hours. The better the grinding the better is the appearance. It must dissolve clear in dilute hydrochloric acid on warming. From, for example, 100 kilos. of aniline, 110–115 kilos. of *p*-nitroaniline are obtained, which is a yield of 74–77·5 per cent. By evaporation of the mother liquors (from which a little *p*-nitroaniline separates) with animal charcoal and several recrystallisations the sodium acetate can be obtained in a commercially useful form.

In order to reduce the cost of manufacture to the lowest possible figure, it is necessary also to recover the sulphuric acid used in the process. This is, of course, contained in the filtrate from the *p*-nitroacetanilide, and is evaporated in a concentration plant.

The Farbenfabriken vorm. F. Bayer & Co. (G.P., 72173) prepares *p*-nitroaniline by nitrating benzylideneaniline (obtained by warming together aniline and benzaldehyde and running off the bottom layer of the benzylidene compound from the water above it).

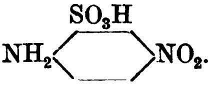
Benzylideneaniline (18·1 kilos.) is added to 70 kilos. of sulphuric acid (66° Bé.), the temperature not being allowed to rise above 50°. The mixture is then cooled and a mixture of 10·8 kilos. of nitric acid (40° Bé.) and 10·8 kilos. of sulphuric acid added at 5–10°. After a short time the mass is poured into an equal volume of water, and the benzaldehyde, which is split off, is driven over with steam. On cooling and diluting with water, *p*-nitroaniline is obtained. Complete separation is effected by neutralising most of the acid with alkali. The product is pure and is obtained in a yield of more than 90 per cent. of the theoretical. The benzaldehyde, which is recovered with very little loss, is used again.

An entirely different process is that patented by the Clayton Aniline Co. (E.P., 24869 of 1902; F.P., 335204; G.P., 148749). *p*-Chloronitrobenzene is heated with excess of strong ammonia under pressure in an autoclave to about 170°. After cooling, the unaltered chloro-derivative is distilled off with steam and the *p*-nitroaniline is filtered and dried. The reaction is facilitated by the addition of metallic copper (Aktiengesellschaft für Anilinfabrikation, E.P., 3966 of 1908; F.P., 397485; G.P., 204951).

p-Nitroaniline melts at 148·3°, and its acetyl compound at 215–216°. Arppe (*Annalen*, 1855, **93**, 357) states that it dissolves in 45 parts of water at 100° and in 1,250 parts at 18·5°; Carnelley and Thomson (*Trans.*, 1888, **53**, 786) give 1,298 parts at 20°; 100 grams of ethyl alcohol dissolve 5·84 grams at 20°. Its density is 1·424.

p-Nitroaniline is used mostly for producing para-red on the fibre, and for Autol red BL, Naphthol blue-black, Diamine (Dianol, Chlorazol) green G, etc.

4-NITROANILINE-2-SULPHONIC ACID,

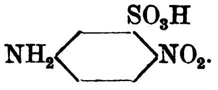


$$\mathrm{NH_2}\overset{\mathrm{SO_3H}}{\bigcirc}\mathrm{NO_2}.$$

This is prepared by heating 2-chloro-5-nitrobenzenesulphonic acid (p. 14) with alcoholic ammonia for two to three hours at 120–140°, and is obtained as the ammonium salt, which is very readily soluble in water (Fischer, *Ber.*, 1891, **24**, 3789).

It is used for making Lake red P and Eriochrome phosphine R.

4-NITROANILINE-3-SULPHONIC ACID,

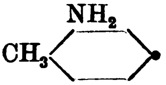


$$\mathrm{NH_2}\overset{\mathrm{SO_3H}}{\bigcirc}\mathrm{NO_2}.$$

Sodium metanilate is acetylated by boiling with twice the theoretical amount of acetic acid and the product is at once dissolved in five times its weight of sulphuric acid. The solution is cooled and a cold mixture of the theoretical amount of nitric acid (D 1·385) with four times its weight of sulphuric acid is run in. After two to three hours the mixture is poured on ice and, after several hours, the yellow product is filtered off and dried.

The acid forms yellow needles moderately soluble in cold, but fairly so in boiling water, and sparingly soluble in alcohol (Eger, *Ber.*, 1888, **21**, 2579). It is used for making nitro-*m*-phenylenediamine.

o-TOLUIDINE,



$CH_3C_6H_4NH_2$

In the early days of the aniline dye industry, the chief requirement for *o*- and *p*-toluidine was for the purpose of making Magenta, and as a mixture of the two was used crude nitrotoluene or even a mixture of nitrobenzene and nitrotoluene was reduced and the product employed directly. Later arose the demand for pure *o*- and *p*-toluidines, and the mixture of toluidines obtained as mentioned above was separated by various means, one of the best being that due to Friswell (*J. Soc. Chem. Ind.*, 1908, **27**, 258), which consisted in mixing the toluidine with crushed ice and filtering off the *p*-toluidine hydrate which was formed, the *o*-toluidine being contained in the filtrate. At a still later date, a considerable demand arose for *o*- and *p*-nitrotoluenes, and it became necessary to make the separation at this stage. This is effected by fractional distillation in a vacuum and is described on p. 33.

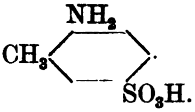
The reduction of *o*-nitrotoluene to *o*-toluidine is carried on in exactly the same way as is the reduction of nitrobenzene to aniline, which is described on p. 40.

For the catalytic reduction, 130 parts of pumice, 25 parts of copper oxalate, and 1 part of magnesium oxide are made into a paste with a little water, and this is dried in an oven, heated to 200°, and a stream of hydrogen passed over it. Then at 200–230° a mixture of *o*-nitrotoluene vapour and excess of hydrogen is led over the mass, when *o*-toluidine and water pass over and are condensed (see Badische Anilin- & Soda-Fabrik, patents on page 44).

o-Toluidine boils at 199·7° and does not solidify at —20°. It has D^4_4 1·1012, D^{15}_{15} 1·0031, D^{25}_{25} 0·997, and D^{50}_{50} 0·9852. It dissolves in water to about the same extent as does aniline. When distilled in steam, 34 grams pass over with 1 kilo. of steam.

It is used for making Magenta, New Magenta, New Methylene-blue, Safranine, Fast acid violet A2R, Immedial indones, Chrysoidine R, Cloth reds, and Sudan IV.

o-TOLUIDINESULPHONIC ACID,



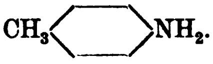
$CH_3C_6H_3(NH_2)SO_3H$

This is prepared like sulphanilic acid (p. 47) by heating *o*-toluidine hydrogen sulphate, $C_7H_7{\cdot}NH_2,H_2SO_4$, in an oven, at 180–200° for several hours (compare Mühlhäuser, *Dingl.*

Polyt. J., 1887, **264**, 244). It crystallises with $1H_2O$ and is sparingly soluble in cold water but readily so in hot. The sodium salt crystallises with $4H_2O$.

o-Toluidinesulphonic acid is used for making Orange R (Orange T).

p-TOLUIDINE,

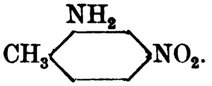


This is prepared by reducing *p*-nitrotoluene in the same way as aniline is manufactured (see p. 40). Care must, however, be taken to keep the pipes warm through which it passes, as it solidifies at a little above 40°.

p-Toluidine melts at 45° and boils at 200·4°/760 mm. and 86–87°/10 mm. Its density is 1·046. It dissolves in 285 parts of water at 11·5°, and when distilled in steam 33 grams pass over with 1 kilo. of steam.

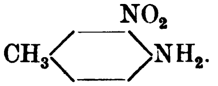
p-Toluidine is used for making dehydrothio-*p*-toluidine and Magenta, Primuline, Fast acid violet B, Alizarin irisol, etc.

p-NITRO-*o*-TOLUIDINE,



See under *p*-Azoxy-*o*-toluidine, p. 99.

m-NITRO-*p*-TOLUIDINE,



This is prepared in an analogous manner to *p*-nitroaniline (p. 51).

Aceto-*p*-toluidide melts at 153° and boils at 307°. The nitro-derivative melts at 94–95°.

m-Nitro-*p*-toluidine melts at 116°. It is used for making Pigment fast red HL (Helio fast red RL, Lithol fast scarlet, Sita fast red RL, Graphitol fast red), and is also brought on the market under its own name and as Pigment fast red base HL, Nitrotoluidine G, or Base HR.

XYLIDINES.

The mixture of nitroxylenes (p. 38) is reduced with iron and hydrochloric acid as in the case of nitrobenzene (see p. 40).

The proportion of the various xylidines occurring in the crude mixture has been variously stated, and the different amounts given are possibly due to variations in the composition of the xylene nitrated. Thus Noelting, Witt, and Forel (*Ber.*, 1885,

18, 2664) state that crude xylidine contains about 25 per cent. of *p*-xylidine, and Witt (*Dingl. Polyt. J.*, 1886, **260**, 95) that it contains this amount of *p*-xylidine and about 75 per cent. of *m*-4-xylidine. On the other hand, Hodgkinson and Limpach (*Trans.*, 1900, **77**, 65) separated the following from commercial xylidine :

m-4-Xylidine	40–42 per cent.
p-Xylidine	30 „
m-2-Xylidine	2·7 „
o-3- and *o*-4-Xylidine	20–25 „

It seems possible that the material investigated by Witt may have been a refined product obtained from crude xylidine by treatment with hydrochloric acid.

The separation is effected as follows :

(1) A mixture containing 60–70 per cent. of *m*-4-xylidine and 30–40 per cent. of *p*-xylidine is obtained by means of hydrochloric acid, whereby the hydrochlorides of these bases crystallise out and are separated from their isomerides by filtering or centrifuging. The bases are obtained from the salts by treatment with alkali and distillation in steam.

(2) One hundred and twenty-one parts of commercial xylidine are mixed with 30 parts of glacial acetic acid ; the crystallisation of the acetate commences at once and is complete after a day or two. The crystals are separated by centrifuging and consist of pure *m*-4-xylidine acetate. The filtrate is mixed with hydrochloric acid (1 mol.) and after some days the hydrochloride of *p*-xylidine is centrifuged (Limpach, E.P., 6899 of 1888 ; F.P., 178616 ; G.P., 39947 ; Hodgkinson and Limpach, *loc. cit.*).

(3) The crude *p*-xylidine (121 parts), obtained after the separation of the *m*-4-xylidine acetate and regenerated from its hydrochloride by treatment with alkali and distillation in steam, is mixed with 106 parts of benzaldehyde. The temperature rises to about 60° and the reaction may be hastened by heating. The warm product is run off from the water which is formed, or the latter is removed by evaporation. The residual oil crystallises on cooling. It is centrifuged and adhering oil removed by washing with alcohol. The benzylidene compound (m. p. 102–103°) is decomposed by dilute hydrochloric or sulphuric acid and the benzaldehyde is driven over with steam to be used again. Sodium hydroxide or milk of lime is now added to the residue until alkaline and the *p*-xylidine is distilled in a current of steam, leaving behind phenyldi-*p*-aminoxylylmethane,

$$C_6H_5{\cdot}CH[C_6H_2(CH_3)_2{\cdot}NH_2]_2,$$

melting at 208°. The oily benzylidene compounds are similarly decomposed into benzaldehyde and crude xylidine (Farbenfabriken vorm. F. Bayer & Co., G.P., 71969).

A xylidine containing the *m*- and *p*-isomerides may be separated by means of formaldehyde in the above manner, as only the *p*-xylidine combines with it, the *m*-xylidine remaining unchanged (Farbwerke vorm. Meister, Lucius, & Brüning, G.P., 87615).

A method of separating *m*-2-xylidine consists in heating the crude xylidine with the necessary quantity of aqueous sulphuric acid to convert it into sulphates, when, on cooling, the sulphates of *m*-4- and *p*-xylidine separate out. These are removed, the mother liquor is evaporated to a syrupy consistency, and the sulphate of *m*-2-xylidine separates on cooling; it is converted into the base in the manner described above (Winkelhausen, G.P., 251334; compare also Hodgkinson and Limpach, *loc. cit.*).

Witt (G.P., 34854) heats 121 kilos. of commercial xylidine with 400 kilos. of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide) at 80–100° to obtain the monosulphonic acids. On pouring into water the sulphonic acid of *m*-xylidine separates out, and is filtered off and washed with cold water. The filtrate is neutralised with milk of lime, filtered, the calcium salt converted into sodium salt, and the solution evaporated. On cooling, sodium *p*-xylidinesulphonate crystallises out. For certain purposes these sulphonic acids can be used direct, otherwise *m*-xylidine is recovered from its sulphonic acid by heating with dilute acids, and *p*-xylidine is obtained by dry distillation of its sodium sulphonate.

Börnstein and Kleemann (G.P., 56322) saturate commercial xylidine with sulphur dioxide, and after cooling and long standing the mass crystallises to yellow needles. These are centrifuged, and the escaping oil is again treated, if necessary, with sulphur dioxide, and the crystals again separated. *p*-Xylidine is obtained from the oil by heating it either alone or with water. The crystals, on being warmed with water, give *m*-xylidine with a little *o*-xylidine. A molecular proportion, or rather more, of hydrochloric acid is added, and, after some time, the hydrochloride of *m*-xylidine crystallises out, whilst the salt of *o*-xylidine remains in solution.

The properties of the xylidines are shown in the following table :—

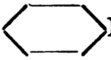
	Constitution.					
Name.	CH_3	CH_3	NH_2	M. p.	B. p.	Specific gravity.
o-3-Xylidine	1	2	3	—	223°/739 mm.	0·991 at 15°
o-4-Xylidine	1	2	4	49°	224°/728 mm.	1·0755 at 17·5°
m-2-Xylidine	1	3	2	—	216°/735 mm.	0·980 at 15°
m-4-Xylidine	1	3	4	—	216°/728 mm.	0·9184 at 25°
m-5-Xylidine	1	3	5	—	220–221°	0·972 at 15°
p-Xylidine	1	4	2	15·5°	213·5°/762 mm.	0·980 at 15°

Crude xylidine is used for making ψ-cumidine and Sudan II, Double scarlet R, Cochineal scarlet 4R, Orange L, Ponceau R, G, GR, and J, and Brilliant ponceau G.

o-Xylidine is used for making Bordeaux BX and Union fast claret (through aminoazoxylene).

m-4-Xylidine is used for making dehydrothio-*m*-xylidine and for Palatine scarlet A, Ponceau 2R, and Resorcine brown.

p-Xylidine is used for making Melogen blue BH, etc.

METHYLANILINE, $NH{\cdot}CH_3$.

The monomethylation of aniline is performed in the same plant as is used for the manufacture of dimethylaniline (see p. 62).

Fifty-five parts of aniline hydrochloride and 16 parts of methyl alcohol are heated for two to three hours at 180°; the pressure rises to 5 atmospheres and later to 25 atmospheres. The pressure is released and the mixture heated for a further six hours at 180°. It is then rendered alkaline with milk of lime and the methylaniline distilled in a current of steam. The yield is about 40 parts of the crude product boiling at 190–191°, which contains 90 per cent. of monomethylaniline, 6–7 per cent. of dimethylaniline, and 1–3 per cent. of aniline.

Another process (Knoll & Co., G.P., 250236) is to heat a mixture of 140 parts of aniline, 32 parts of methyl alcohol, and 1 part of iodine for ten hours at 220°.

Geigy & Co. (F.P., 212506; G.P., 75854) condense aniline with formaldehyde and then reduce the anhydroformaldehydeaniline (methyleneaniline) to methylaniline with zinc and sodium hydroxide.

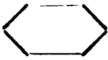
An improvement on this method has been patented by Morgan (E.P., 102834 [1916]; F.P., 485282; U.S.P., 1221077), who finds it much more advantageous to carry on both reactions simultaneously. His process is as follows: Sixty parts of aniline and 66 parts of 40 per cent. formaldehyde are added slowly and concurrently to 300 parts of 34 per cent. sodium hydroxide solution

(D 1·37) containing 90 parts of zinc dust in suspension. The addition of the reagents should take about two hours and the mixture should be well stirred and kept at 90°. The heating and stirring are continued for six hours longer, during which 40 parts of 40 per cent. formaldehyde are slowly added. When the percentage of methylaniline has reached a maximum, the mixture is distilled with steam and the methylaniline obtained from the distillate in any of the usual ways.

Methylaniline is also produced, along with dimethylaniline, by passing the vapours of aniline and methyl alcohol over aluminium oxide at 400–430° (Mailhe and de Godon, *Compt. rend.*, 1918, **166**, 467).

A mixture of methylaniline and aniline can be separated by the process described on page 71, under Ethyl-*o*-toluidine.

Methylaniline boils at 192° or 95°/25 mm. and has D^{15} 0·976. On ethylation, it yields methylethylaniline, b. p. 201° (Claus and Howitz, *Ber.*, 1884, **17**, 1324). It is used for making benzylmethylaniline.

DIMETHYLANILINE,  $N(CH_3)_2$.

Dimethylaniline is prepared by heating together aniline and methyl alcohol with a little sulphuric acid in an autoclave. A detailed description of the manufacture is given by Walter* (*Chem. Zeit.*. 1910, **34**, 641, 667, 681, 690).

The autoclaves are of 280 litres capacity and are protected from the action of acid by means of a lining made of enamelled cast iron or of special acid-resisting metal. The space between the autoclave and the lining is filled with lead (the metal-bath is heated while this is filled in), and the autoclave is set in a metal-bath of cast iron filled with fusible metal (70 per cent. lead and 30 per cent. tin). This is scarcely required if gas heating is employed. Fig. 16 shows the general arrangement of the plant and Fig. 17 the setting of an autoclave and still, etc.

Each autoclave is charged in the morning with 80 kilos. of aniline, 78 kilos. of methyl alcohol (which must be free from acetone), and 8 kilos. of sulphuric acid (66° Bé.). The alcohol is weighed out the day before into two carboys, and to each of these 4 kilos. of sulphuric acid are slowly added through a glass funnel. The aniline is also previously weighed out into two iron drums. When filling the autoclave, a drum of aniline is first put in, then

* This long paper, containing many diagrams, should be consulted if a plant is to be erected.

the two carboys of methyl alcohol, and, lastly, the second drum of aniline. The charging is finished at 10 a.m. and the autoclave is heated gradually to 230–235°, the thermometer being in the metal-bath. About 2 p.m. the full pressure is reached at 28–30 or even 32 atmospheres, which remains constant for about three hours and then falls off slightly. At 11 p.m. the fire is drawn, the fire-doors are opened, and also the four side flue-doors. If time permits, the autoclave is allowed to cool over the following day; if not, at 6 a.m. next morning the tap on the autoclave, which is connected with a pipe leading the gases and vapours to a condenser, is opened slowly. The gases coming from this condenser, which consist chiefly of methyl ether, pass through a column of water about 60 cm. high before being led into the open; this water also retains some methyl alcohol. After this "blowing off," the pipe screwed into the lid, which carries the tap and manometer, is unscrewed and a copper pipe screwed in its place. This pipe reaches to the bottom of the autoclave and is connected with the still for the dimethylaniline. The safety valve is also removed and replaced by a right-angled pipe to which connexion is made with the compressed air supply. In the meantime, the

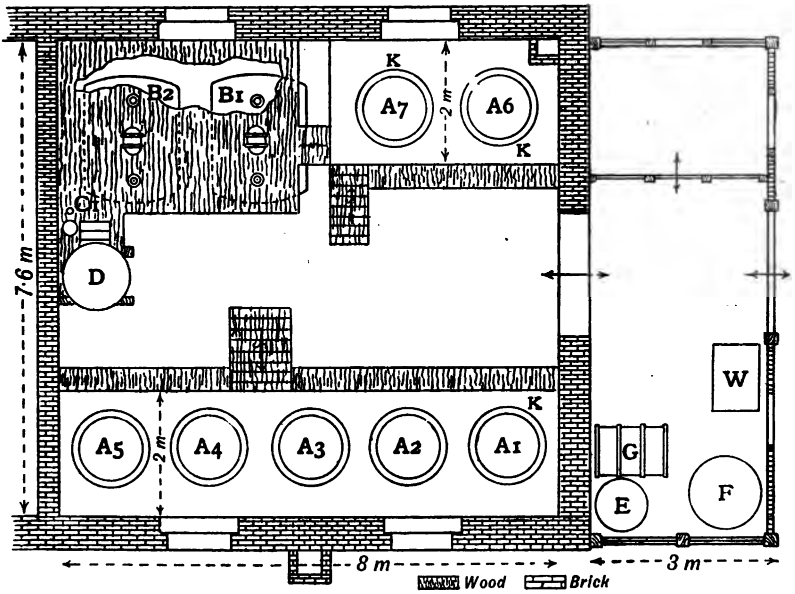


FIG. 16.

amount of sodium hydroxide necessary to neutralise the contents of five or six autoclaves has been dissolved in a little water, and now the finished batches are blown over from the autoclaves and mixed by blowing in a little steam. As soon as this is done, steam

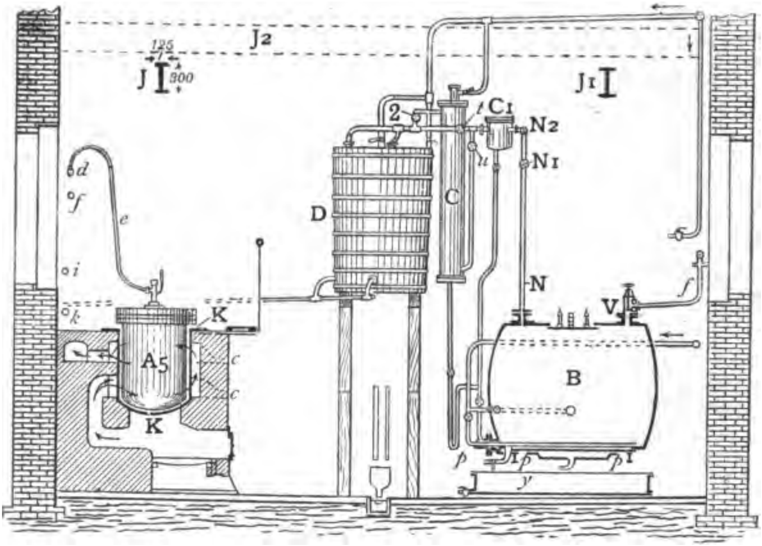


Fig. 17.

Arrangements of Dimethylaniline Plant (Figs. 16 and 17).

A_1 to A_7, the autoclaves; B1 and B2, the two stills; C, small condenser; C1, water separator; D, large condenser; E, small condenser for methyl alcohol; F, separator (1,000 litres) for dimethylaniline and water; G, drum for collecting methyl alcohol (a similar drum is placed outside the building for collecting dimethylaniline); K, metal-bath for autoclaves; W, scales.

Additional to Fig. 17 are: *c*, dampers on right and left of fire-door; *e*, narrow-bore copper tube leading gases from autoclave to copper pipe *d*; *f*, copper pipe, 60 mm. diam., fixed on wall behind autoclaves leading into B through the valve V; *i*, compressed-air pipe; *k*, pipe for condensed water; *p*, steam jacket round lower half of B; N, pipe for steam exit from B, closed by tap N1; pipes N from both stills lead into the pipe N2 connected to C1, from which any water carried over runs back to B; the vapours pass on to D either direct or through *c*; from *c* the condensate returns to B through a siphon tube. *c* is used only at the beginning of the distillation for the recovery of methyl alcohol, when taps 2 and *u* are open and *t* is shut; J, J1, and J2 are iron rails carrying pulley blocks to lift the lids, pans, etc.; *y* is a wrought iron pan into which the liquor from the still is run at the end of the distillation. The pipe entering B on the right is for steam, and that shown at the top right-hand corner for water.

is led into the steam jacket of the still (1·5 metres in diameter and 1·6 metres long) and methyl alcohol and gas pass through the condenser and water-column. Some of these gases will have also passed through the condenser during the blowing over process. Steam is now led inside the still and dimethylaniline and methyl alcohol distil over with the steam. A small condenser leads the condensed water and dimethylaniline back to the still while the methyl alcohol vapours pass through it into the large condenser. Distillation is carried on slowly until drops of dimethylaniline rise quickly in a sample of the distillate. The small condenser is now shut off and the vapours are led directly into the large one (which contains a lead coil). The distillate is also now collected in a different receiver (1,000 litres) and the steam supply to the still is increased. This distillate, consisting of water and dimethylaniline, rapidly separates into its constituents (1 part of oil to 6 parts of water), and the dimethylaniline is collected in iron drums whilst the water runs away.

As soon as only a small amount of dimethylaniline passes over with the steam, the steam inlet is shut as well as the outlet from the still and the steam valve on the jacket opened. The pressure inside the still rises to 5 atmospheres and is kept at this for 1½ hours. The dimethylaniline remaining is then driven completely over.

The work on the still occupies two days. If 7 autoclaves are worked daily it is necessary to work the two stills night and day.

From the weighed iron drums the dimethylaniline is blown into a 4,000-litre cast iron reservoir, where it is mixed, sampled, and again run into drums. In this reservoir any water entangled with the oil separates out.

The methyl alcohol is rectified and used over again. The yield is 98 kilos. of dimethylaniline, which is 94 per cent. of the theory or 122·5 per cent. of the aniline. With good working, this yield can be increased.

The amount of steam used may be reckoned as 18 parts for 1 part of dimethylaniline.

Paul (*Zeitsch. angew. Chem.*, 1897, **10**, 22) gives the following details. One hundred kilos. of aniline, 96·5 kilos. of methyl alcohol, and 18–19 kilos. of sulphuric acid (64·5° Bé.) are heated for seven hours at 200–210°. Forty kilos. of sodium hydroxide solution (40° Bé.) are required to neutralise the product, and the yield is 125 kilos. of dimethylaniline, and 12–14 kilos. of methyl alcohol are recovered.

Older descriptions of the manufacture of dimethylaniline by the use of hydrochloric acid instead of sulphuric acid have been published by Schoop (*Chem. Zeit.*, 1887, **11**, 253) and by Mühlhäuser (*Dingl. Polyt. J.*, 1887, **263**, 348), but the use of hydrochloric acid is now discontinued. It may, however, be noted that diethylaniline must be made with hydrochloric acid.

Methyl chloride is used as a methylating agent by the firm Vve. Brigonnet et Fils at Saint-Denis, and the process is as follows (Grandmougin, *Rev. prod. chim.*, 1917, **20**, 68).

An autoclave fitted with a stirrer (125–130 revolutions per minute) and set in a water-bath is charged with 50 kilos. of aniline and milk of lime (40 kilos. of quicklime slaked to 75 litres) and heated to 100°. Sixty-two kilos. of methyl chloride are now added during 2–2½ hours, the pressure being kept at 5–6 atmospheres. When the reaction is finished the pressure falls to 2½ atmospheres, when it is released and the contents of the autoclave are blown to a still, where the dimethylaniline is distilled with steam.

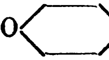
The yield is 116–120 per cent. of the weight of aniline employed. Two methylations can easily be made in a day.

A recent patent (Knoll & Co., G.P., 250236) describes the preparation of dimethylaniline by heating a mixture of aniline (93 parts), methyl alcohol (96 parts), and iodine (1 part) for seven hours to 230°. The product is separated from water and, after removing iodine with alkali, distilled in a vacuum. A quantitative yield is said to be obtained by this process.

Dimethylaniline is also obtained, mixed with monomethylaniline, when a mixture of the vapours of aniline and methyl alcohol is passed over aluminium oxide at 400–430°. By this catalytic process monomethylaniline is similarly converted into dimethylaniline (Mailhe and de Godon, *Compt. rend.*, 1918, **166**, 467).

Dimethylaniline boils at 192·6°/738 mm. or 100°/34 mm., melts at 0·5°, and has D^{15} 0·96. It is much less soluble in water than is aniline.

It is used for the manufacture of Methyl violet, Malachite green, Methylene blue, Meldola's blue, Methyl orange, etc.

p-Nitrosodimethylaniline, NO  $N(CH_3)_2$.

Twenty-six kilos. of dimethylaniline are mixed with 100 kilos. of hydrochloric acid (31 per cent.) and 100 kilos. of ice, whereby the temperature falls to −15°. A solution of 16 kilos. of sodium nitrite in 35 litres of water is now run in underneath the surface by means of a glass tube (lead may also be used), and at the end the temperature will have risen to about 5° (Walter, "Aus der Praxis der Anilinfarbenfabrikation," 1903.) The tub in which the operation is carried out should contain no metal nails or fittings. The end-point is ascertained with starch-iodide paper. The yellow hydrochloride is filtered off (out of contact with metal), washed, and dried. The hydrochloride melts at about 177° and the base at 92°.

p-Nitrosodimethylaniline (as hydrochloride) is used for making Capri blue, Gallocyanine, Prune pure, Gallamine blue, Gallanil violet, Nitroso blue MR, Meldola's blue (Cotton blues), New blue B, Muscarine, Fast black, Methylene blue, Neutral violet, Neutral red, Fast neutral violet B, Methylene grey, Safranine MN, Rhoduline violet, Tannin heliotrope, Indazine, Metaphenylene blues, and Naphthazine blue, and also comes on the market as Nitroso base M.

ETHYLANILINE,

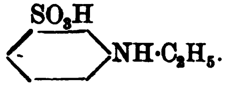
Ninety-five parts of aniline hydrochloride and 28 parts of ethyl alcohol are heated together in an enamelled autoclave (see under Dimethylaniline, p. 62) at 180° for some hours. The product contains 70–73 per cent. of monoethylaniline which crystallises out as hydrochloride.

An alternative method is to boil a mixture of 130 grams of aniline hydrochloride and 200 grams of diethylaniline under a reflux condenser for six to eight hours. The mixture of bases is dissolved in hydrochloric acid and the solution evaporated until crystallisation begins. The hydrochloride of monoethylaniline separates out, whilst that of diethylaniline remains in solution (compare Blume and Klöffler, *Ber.*, 1905, **38**, 3276).

A mixture of ethylaniline and aniline can be separated by the process described on page 71, under Ethyl-*o*-toluidine.

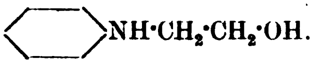
Ethylaniline boils at 206°/760 mm. or 102°/34 mm. and has D^{18} 0·954. On methylation it yields methylethylaniline, b. p. 201° (Hofmann, *Annalen*, 1850, **74**, 152; Claus and Howitz, *Ber.*, 1884, **17**, 1324), and on benzylation, benzylethylaniline.

ETHYLANILINE-*m*-SULPHONIC ACID,



See under Monoethyl-*m*-aminophenol, p. 120.

HYDROXYETHYLANILINE,



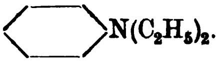
$C_6H_5 \cdot NH \cdot CH_2 \cdot CH_2 \cdot OH$.

This is prepared by boiling a mixture of 186 parts of aniline, 200 parts of water, and 80 parts of ethylenechlorohydrin for two hours under a reflux condenser. The mixture is then rendered alkaline and the excess of aniline distilled off by means of a current of steam (Badische Anilin- & Soda-Fabrik, E.P., 13956 of 1904; F.P., 350002; G.P., 163043; U.S.P. 778772). Otto (*J. pr. Chem.*, 1891, [ii] **44**, 17), who heated 10 grams of ethylenechlorohydrin with 22 grams of aniline for sixteen minutes, obtained a yield of about 70 per cent. of the theoretical. The yield is not so good when equivalent quantities are used, as diethylenedianiline and other by-products are formed (Knorr, *Ber.*, 1889, **22**, 2092).

Hydroxyethylaniline boils at 286° or 167°/17 mm. and has D^0 1·110; it is very sparingly soluble in water, but readily so in alcohol, ether, or chloroform.

It is used for making Indigo.

DIETHYLANILINE,



$C_6H_5 \cdot N(C_2H_5)_2$.

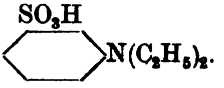
This may be prepared like dimethylaniline, using aniline hydrochloride and ethyl alcohol. Sulphuric acid cannot be employed. The product, however, contains a considerable amount of monoethylaniline, and an improved method of preparation is due to Städel (G.P., 21241), which consists in heating aniline hydrobromide with $2\frac{1}{5}$ molecules of ethyl alcohol at 145–150°.

According to Knoll & Co. (G.P., 250236), 93 parts of aniline, 138 parts of ethyl alcohol, and 1 part of iodine are heated for ten hours to 235°. The product is separated from water, and, after removing iodine with sodium hydroxide, is distilled in a vacuum. The yield is said to be quantitative.

Diethylaniline melts at −38·1°, boils at 216·5°, and has D^{18} 0·939.

It is used for making Brilliant green, Patent blue V (Acid blue G), and Ethyl purple 6B.

DIETHYLANILINE-*m*-SULPHONIC ACID,



$SO_3H \cdot C_6H_4 \cdot N(C_2H_5)_2$.

See under Diethyl-*m*-aminophenol, p. 122.

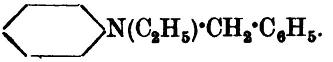
BENZYLMETHYLANILINE,

$N(CH_3)\cdot CH_2\cdot C_6H_5$.

Wedekind (*Ber.*, 1899, 32, 519) heated a mixture of 32·1 grams of methylaniline and 37·9 grams of benzyl chloride on the water-bath for 2½ hours. The hydrochloride was decomposed by concentrated aqueous sodium hydroxide, the oil separated, dried over sodium sulphate and fractionated under 41 mm. pressure. After collecting two small fractions up to 170°, the three next fractions (170–190°, 190–198°, and 198–203°), weighing 29·9 grams, were mixed and redistilled under 60 mm. pressure. After the first runnings up to 205° had been collected the next two fractions (205–210° and 210–212°) consisted of pure benzylmethylaniline (24·4 grams).

Benzylmethylaniline boils at 305–306° or at 210°/60 mm., and is used for making Light green SF bluish and Acid violet 4BN.

BENZYLETHYLANILINE,



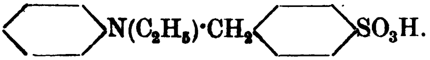
$N(C_2H_5)\cdot CH_2\cdot C_6H_5$.

This is prepared by boiling 1 part of monoethylaniline and 2 parts of benzyl chloride under a reflux condenser for four hours (Stebbins, *J. Amer. Chem. Soc.*, 1885, 7, 42). The product is fractionated, and after the excess of benzyl chloride and a little ethylaniline have distilled over the benzylethylaniline is collected.

Benzylethylaniline boils at 286°/710 mm. (uncorr.), or 185·5 186·5°/22 mm. and has $D^{18\cdot5}$ 1·034.

It is used for making Light green SF yellowish, Xylene blue AS, Erioglaucine, and Patent blue A (Neptune blue B, Brilliant acid blue A).

BENZYLETHYLANILINESULPHONIC ACID.



$N(C_2H_5)\cdot CH_2\cdot C_6H_4\cdot SO_3H$.

Fifty kilos. of benzylethylaniline are added to 120 kilos. of fuming sulphuric acid (containing 21 per cent. of sulphur trioxide) at 40–50° and the mixture is kept at this temperature until a sample dissolves readily in dilute sodium hydroxide. One hundred kilos. of water are now added, care being taken that the temperature does not rise above 50°. The acid can also be precipitated, below 50°, by adding 100 kilos. of sodium hydroxide solution (40 per cent.). It is then filtered, pressed, and dried (Aktiengesellschaft für Anilinfabrikation, E.P., 7550 of 1889; F.P., 198415; G.P., 50782).

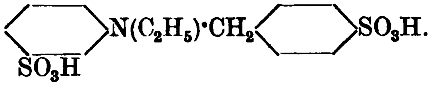
An alternative process is to heat 22 kilos. of benzylethylaniline with 88 kilos. of sulphuric acid (100 per cent.) at 180° until a sample is soluble in alkali. Five hundred litres of water are carefully added and the acid is worked up as described above (Geigy, E.P., 21284 of 1890; G.P., 59811).

Gnehm and Schönholzer (*J. pr. Chem.*, 1907, [ii], **76**, 489) heated the amine with 4–5 parts of sulphuric acid (100 per cent.) at 110–120° for about two hours, when they found the sulphonation to be complete.

The acid is sparingly soluble in cold water, but crystallises from hot water with $1H_2O$ (Gnehm and Schönholzer, *loc. cit.*), and can be salted out of solution. The salts are readily soluble in water. The sodium salt crystallises with $3H_2O$.

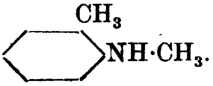
The acid is insoluble in alcohol, but the sodium salt can be crystallised from the hot solvent. The potassium salt is sparingly soluble in cold but readily so in hot alcohol. The compound is used for making Azocardinal G, Night green A (Neptune green SG), Formyl violet S4B, Acid violet 6B, Thiocarmine R, Guinea green B, and Erioglaucine A.

BENZYLETHYLANILINEDISULPHONIC ACID,



Ten kilos. of benzylethylaniline are added slowly to 20 kilos. of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide) with cooling, and when all is dissolved 25 kilos. of fuming sulphuric acid (containing 80 per cent. of sulphur trioxide) are added and the mixture is warmed at 60° until the sulphonation is complete. The mass is poured into water, neutralised with milk of lime, the calcium sulphate filtered off, and the calcium salt treated with sodium carbonate. After filtering from the calcium carbonate the solution is saturated with salt, whereby the sodium salt of the disulphonic acid is obtained (Farbenfabriken vorm. F. Bayer & Co., E.P., 19062 of 1891; F.P., 217020; G.P., 69777). The acid is used for making Fast acid violet 10B.

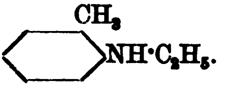
METHYL-*o*-TOLUIDINE,



This was prepared by Monnet, Reverdin, and Noelting (*Ber.*, 1878, **11**, 2278) by heating a mixture of 750 grams of *o*-toluidine, 400 grams of methyl alcohol, and 700 grams of hydrochloric acid for a day at 200–220°. For more modern methods of methylation and for the process of working up, see under Methylaniline (p. 61).

Methyl-*o*-toluidine boils at 207–208° and has D^{15} 0·973. It is used for making dimethyldiaminodi-*o*-tolylmethane and for Glacier blue and Brilliant rhoduline red B.

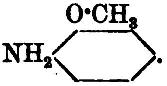
ETHYL-*o*-TOLUIDINE,



This is prepared in the same way as methyl-*o*-toluidine (above), substituting ethyl alcohol for methyl alcohol (compare also the process for ethylating aniline, p. 67). The technical product usually contains 10–15 per cent. of *o*-toluidine, and this can be separated by adding to the mixture an amount of sulphuric acid (96 per cent.) sufficient to combine with the primary amine, allowing to cool, removing the sulphate of the latter by filtering or centrifuging, and washing the precipitate with benzene or alcohol (Price, *J. Soc. Chem. Ind.*, 1918, **37**, 84T).

Ethyl-*o*-toluidine boils at 213–214° and has $D^{15\cdot5}$ 0·9534. It is used for making Cyanol and New methylene blue.

o-ANISIDINE,



To a mixture of equal parts of *o*-nitroanisole (p. 96) and hydrochloric acid warmed to 90° the calculated amount of finely ground iron is added sufficiently rapidly to cause the temperature to rise to 100–110°. Water distils through the condenser and is returned to the mixture from time to time. When all the iron has been added, stirring is continued until the temperature falls to 90°. More water is then added, the reduction mixture rendered alkaline with sodium hydroxide solution, filtered through a filter press, and the iron residue washed with alcohol until all the *o*-anisidine has been extracted. The alcohol is distilled off and the base united with the main amount and distilled in a vacuum (Heumann, " Die Anilinfarben, etc.," IV, i, 310).

The reduction may also be carried out with tin and hydrochloric acid (Mühlhäuser, *Annalen*, 1881, **207**, 238).

o-Anisidine can also be prepared by heating *o*-aminophenol (1 mol.), potassium methyl sulphate (2 mols.), and potassium hydroxide solution (2 mols.) in an autoclave for eight to ten hours at 170°. The *o*-anisidine is obtained by distilling the product in a current of steam, the yield being 70 per cent. of the theoretical.

o-Anisidine melts at 2·5° and boils at 218°/755·5 mm. It is used for making Chrome fast yellow GG, Pigment purple A, Buffalo flamine G (Azoeosine G), and Azocochineal.

DIPHENYLAMINE,

This is prepared by heating a mixture of aniline and aniline hydrochloride (Girard and de Laire, "Traité des dérivés de la houille," 1873, p. 418) in an autoclave fitted with an enamelled lining or one made of special acid-proof metal, and heated in a bath of fusible metal (for example, 30 per cent. of tin and 70 per cent. of lead), or the autoclave may be heated directly by gas.

Seventy kilos of dry aniline hydrochloride and 50 kilos. of aniline are heated gradually to 260°, which temperature is maintained for twelve hours, the ammonia being allowed to escape from time to time. The pressure is about 5 atmospheres, and the whole operation takes about twenty-four hours. After cooling, the contents of the autoclave are transferred to a tub and heated with concentrated hydrochloric acid. If now water is added, the aniline hydrochloride remains in solution and the hydrochloride of diphenylamine is dissociated. The solution is drawn off and the aniline recovered from it, whilst the cake of diphenylamine is boiled with water, then with dilute sodium carbonate, and finally with water. It is finally distilled with superheated steam, or dried and distilled in a vacuum. In the latter case, a little water and aniline pass over first, and then the diphenylamine distils over. Alternatively, the contents of the autoclave can be poured into water to remove aniline hydrochloride and ammonium chloride, and the aniline and diphenylamine separated by fractional distillation. The yield is about 70 kilos., or 80 per cent. of the theoretical.

A process which can be carried out without the use of an autoclave is described by Goldberg (*Ber.*, 1907, **40**, 4541; E.P., 2766 of 1907 [Aktiengesellschaft für Anilinfabrikation]; F.P., 374385; G.P., 187870).

Forty parts of acetanilide and 48 parts of bromobenzene are dissolved in nitrobenzene and 15 parts of potassium carbonate and 1 part of cuprous iodide added. The mixture is heated to
ing point in a reflux apparatus for ten hours and then the
is fractionally distilled in a current of steam to remove

nitrobenzene and bromobenzene. The residue is hydrolysed to diphenylamine.

According to Flürscheim (U.S.P., 1212928), the use of an enamelled autoclave can be avoided by using ferric chloride instead of hydrochloric acid. A mixture of 430 parts of ferric chloride ($FeCl_3,6H_2O$), 892 parts of aniline, 44·5 parts of finely divided copper, and 4·5 parts of iodine is heated gradually to 238°. The pressure is released when it reaches 110 lb., the temperature being lowered to 180° previously. The heating is continued for about twenty hours at 238–240°. The diphenylamine is then separated from aniline in the usual way.

Diphenylamine melts at 54°, boils at 310°, and has D 1·16.

It is used for the manufacture of Orange IV., Metanil yellow, Helvetia blue, and certain sulphur blues.

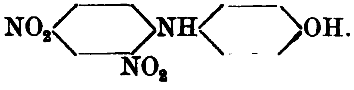
METHYLDIPHENYLAMINE, (DIPHENYLMETHYLAMINE)

This is prepared by heating a mixture of 100 kilos. of diphenylamine, 68 kilos. of hydrochloric acid (D 1·17), and 24 kilos. of methyl alcohol for ten hours in an enamelled autoclave at 200–250°, under a pressure of 10–15 atmospheres (see Dimethylaniline, p. 62). After cooling, sodium hydroxide is added, and the bases are separated and distilled. The methyldiphenylamine is separated from diphenylamine by treating with twice the volume of hydrochloric acid and filtering off the liquid hydrochloride of the former from the solid hydrochloride of the latter, which crystallises out on cooling. The methyldiphenylamine hydrochloride is dissociated by water and the free base purified by distillation (Girard, *Bull. Soc. chim.*, 1875, [ii], **23**, 2).

Methyldiphenylamine is an oil which boils at 282° and has D^{20}_{4} 1·0476.

It is used for making Alkali and Acid violets.

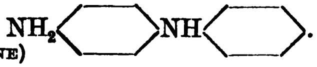
2 : 4-DINITRO-4′-HYDROXYDIPHENYLAMINE,



4-Chloro-1 : 3-dinitrobenzene and *p*-aminophenol, in molecular proportions, are boiled in aqueous suspension with slightly more than the theoretical quantity of chalk. The mixture is well stirred and the vessel is fitted with a reflux condenser, the heating being effected by direct steam. The chloronitrobenzene melts, and when it has disappeared the liquid is cooled, and the crystalline condensation product which separates is collected and washed (Lange, "Die Schwefelfarbstoffe," 1912, p. 146).

2 : 4-Dinitro-4′-hydroxydiphenylamine melts at 190° and is used for making 3-amino-7-hydroxyphenazine and Immedial black, Immedial blue, Immedial brown, and Pyrogen blue.

p-AMINODIPHENYLAMINE,



(PHENYL-*p*-PHENYLENEDIAMINE)

This is conveniently prepared by reducing Orange IV (prepared from diazotised sulphanilic acid and diphenylamine) with a solution of sulphur in sodium sulphide.

77·5 Kilos. of Orange IV are mixed with 600 litres of boiling water; a mixture of 12 kilos. of flour of sulphur, 70 kilos. of crystallised sodium sulphide, 5 kilos. of sodium hydroxide, and 120 litres of boiling water is added, and the whole heated under a pressure of two atmospheres. The insoluble *p*-aminodiphenylamine is then separated by filtration (Cobenzl, *Chem. Zeit.*, 1915, **39**, 859). The yield is 90 per cent.

Ullmann and Dahmen (*Ber.*, 1908, **41**, 3744) prepared it as follows:

25·9 Grams of sodium 2-chloro-5-nitrobenzenesulphonate (from *p*-chloronitrobenzene), 25 grams of glycerol, and 5 grams of calcium carbonate are mixed with 78 grams of aniline and heated in an oil-bath at 180–185°, a reflux condenser being used. The mass becomes first yellow and then reddish-brown and the condensation is finished in eight hours. The product is diluted with water, 10 grams of sodium carbonate are added, and the excess of aniline (66 grams) is distilled off with steam. From the filtered solution 28·7 grams of sodium *p*-nitrodiphenylamine-*o*-sulphonate separate out, and 2 grams of unchanged sodium 2-chloro-5-nitrobenzenesulphonate are recovered by concentrating the mother liquor. The yield is thus 98·4 per cent. of the theoretical.

The elimination of the sulphonic group is effected by warming with either hydrochloric acid or dilute sulphuric acid, and the yield is increased by thorough stirring.

7·9 Grams of sodium *p*-nitrodiphenylamine-*o*-sulphonate are warmed on the water-bath under reflux with 30 c.c. of hydrochloric acid (D 1·12). The yellow crystals soon disappear, and the free nitrodiphenylaminesulphonic acid separates as a brownish-red oil which also gradually gives place to crystalline *p*-nitrodiphenylamine. At the end of five hours the mass is diluted with water, the brownish-yellow *p*-nitrodiphenylamine filtered off, triturated with a little ammonia, filtered, washed, and dried. The yield is 5 grams, or 93·5 per cent. of the theoretical. If the mixture is heated to boiling, the reaction is ended after two hours and the yield rises to 5·25 grams, or 98 per cent. of the theoretical. When 50 per cent. sulphuric acid is used instead of hydrochloric acid and the mixture boiled under reflux for ten to fifteen minutes (or warmed on the water-bath with 10 parts of 40 per cent. sulphuric acid for two to three hours), the sulphate of nitrodiphenylamine separates as a dark brown, oily mass which, when treated with water, gives 5·1 grams of nitrodiphenylamine. The sulphonic group may also be removed by heating the acid with 10 parts of 60 per cent. sulphuric acid for six to eight hours in the water-bath (Aktiengesellschaft für Anilinfabrikation, E.P., 14167 of 1907; F.P., 379949; G.P., 193448). The pure nitro-compound melts at 132°.

For the reduction, 5·35 grams of the nitro-compound are dissolved in 8 c.c. of 50 per cent. alcohol containing 0·5 gram of ammonium chloride, the solution is boiled under reflux, and 7 grams of zinc dust are gradually added. The yellowish-brown solution finally becomes colourless. A few drops of sodium hydrogen sulphite solution are added and the solution is filtered into 50 per cent. sulphuric acid, when the insoluble sulphate of aminodiphenylamine is precipitated. The yield is 5·3 grams, or 91 per cent. of the theoretical. The base can be obtained by treating the sulphate with water and a little ammonia.

The yield is not quite so good if the solution of sodium *p*-nitrodiphenylamine-*o*-sulphonate, after distilling off the aniline, is exactly neutralised and boiled with 28 grams of iron powder and 1 c.c. of hydrochloric acid, the *p*-aminodiphenylamine-*o*-sulphonic acid* obtained by adding sodium carbonate and a little sodium hydrogen sulphite and filtering into 80 c.c. of hydrochloric acid (D 1·12), and the sulphonic acid group eliminated by boiling the acid (5·3 grams) with 0·25 gram of stannous chloride and 25 c.c. of hydrochloric acid (D 1·12) for ten hours, the sulphate of the base being isolated by the addition of sodium sulphate. The sulphonic group is eliminated on the large scale by heating the acid with 10 parts of 60 per cent. sulphuric acid for six to eight hours in the water-bath. The product is diluted with water and neutralised with alkali (Aktiengesellschaft für Anilinfabrikation, E.P., 14167 of 1907; F.P., 379949; G.P., 193351).

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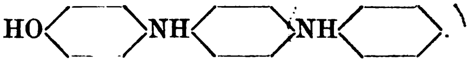
* This is also formed by boiling *p*-nitrosodiphenylamine with sodium hydroxide and sodium sulphite solutions (Badische Anilin- & Soda-Fabrik, G.P., 77536).

p-Nitrodiphenylamine is prepared as follows: Iodine (0·1 part) is dissolved in 10 parts of *p*-chloronitrobenzene, 0·3 part of finely divided copper is added, and the mixture heated until the coloration due to cuprous iodide appears. Then 75 parts of aniline and 5 parts of potassium carbonate are added and the whole is heated under reflux for twenty hours. The mass is acidified with hydrochloric acid, the unchanged *p*-chloronitrobenzene driven over with steam, and the residual crude *p*-nitrodiphenylamine is crystallised from benzene or alcohol.

Alternatively, a mixture of 12 parts of *p*-chloronitrobenzene, 7 parts of aniline, 75 parts of nitrobenzene, 0·2 part of cuprous iodide, and 5 parts of potassium carbonate is heated in an oil-bath for twenty hours to 200–210°. The volatile substances are removed by means of a current of steam and the remaining *p*-nitrodiphenylamine is worked up as above (Aktiengesellschaft für Anilinfabrikation, E.P., 24091 of 1906; F.P., 381230; G.P., 185663).

p-Aminodiphenylamine melts at 75° and boils at 354° (in an atmosphere of hydrogen). It is used for making Rosolan and comes on the market as Diphenyl black base P (Diphenyl black oil DO is a mixture of 25 parts of *p*-aminodiphenylamine and 75 parts of aniline) and as Fast blue developer AD. The *o*-sulphonic acid is used in the production of the Nerol dyes.

4-PHENYLAMINO-4′-HYDROXYDIPHENYLAMINE,



This is prepared by oxidising a mixture of *p*-aminodiphenylamine and phenol or a mixture of diphenylamine and *p*-aminophenol, or by reducing the indophenol obtained by condensing diphenylamine with *p*-nitrosophenol in 80 per cent. sulphuric acid. The latter is, perhaps, the best method.

(1) 18·5 Kilos. of *p*-aminodiphenylamine are dissolved in 300 litres of water and 12·5 kilos. of hydrochloric acid (20° Bé.); 9·4 kilos. of phenol dissolved in 200 litres of water are added, and a solution of 20 kilos. of sodium dichromate in 200 litres of water mixed with 60 kilos. of acetic acid (50 per cent.) is introduced into the well-cooled solution. When the oxidation is complete, the mixture is rendered alkaline by the addition of sodium carbonate, and 75 kilos. of crystallised sodium sulphide are added. The solution is heated for some time to 40–50°, then heated to boiling and filtered. On cooling the filtrate,

4-phenylamino-4′-hydroxydiphenylamine separates in silvery, shining crystals.

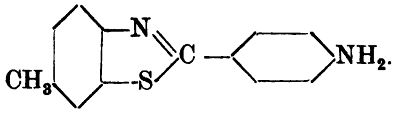
(2) 10·7 Kilos. of *p*-aminophenol and 17 kilos. of diphenylamine are dissolved in 400–500 litres of alcohol; the solution is cooled and a mixture of a solution of 20 kilos. of sodium dichromate and 72 kilos. of hydrochloric acid (20° Bé.) is gradually run in. When the oxidation is complete, 12 kilos. of zinc dust are added, and dilute hydrochloric acid gradually, the solution being cooled, until the solution is decolorised. The alcohol is then distilled off, and the phenylaminohydroxydiphenylamine is obtained from the residue by extraction with boiling dilute sodium sulphide solution (Cassella & Co., E.P., 16823 of 1902; F.P., 323202; G.P., 150553; U.S.P., 723154).

(3) Fifty-one kilos. of diphenylamine are dissolved in 500 kilos. of sulphuric acid (75 per cent.), the solution is cooled to 20°, and 38 kilos. of *p*-nitrosophenol are added gradually, so that the temperature does not exceed 25°. After stirring for five hours, the mass is poured on ice and the product filtered off and washed with water. The paste is stirred with water, 50 kilos. of sodium hydroxide solution (30 per cent.) and 50 kilos. of crystallised sodium sulphide are added, and the whole is stirred for two hours while cooling. The blue colour becomes light brown, and the 4-phenylamino-4′-hydroxydiphenylamine is precipitated by adding 100 kilos. of hydrochloric acid. By re-dissolving in sodium hydroxide solution and adding salt, it may be obtained in a crystalline condition (Society of Chemical Industry in Basle, E.P., 7025 of 1903; F.P., 330388; G.P. Anm. G., 18017; U.S.P., 727387).

4-Phenylamino-4′-hydroxydiphenylamine is almost insoluble in cold, and very sparingly soluble in hot, water. It is readily soluble in alcohol, but rather sparingly so in benzene. The alkali solutions turn blue in contact with air.

It is used for making Pyrogen indigo.

DEHYDROTHIO-*p*-TOLUIDINE,



This base is obtained by heating together 214 parts of *p*-toluidine and 64 parts of sulphur. The temperature is gradually raised to the boiling point and maintained there for several hours. The operation is carried out in the plant described on p. 78. When finished, the melt is fractionally distilled in a vacuum.

The excess of *p*-toluidine and a little diaminoditolyl sulphide pass over first and are then followed by pure dehydrothio-*p*-toluidine which crystallises on cooling (Green, "Dictionary of Applied Chemistry," Thorpe, 1913, IV, 386: compare Farbenfabriken vorm. F. Bayer & Co., E.P., 6319 of 1888; G.P., 50525).

Another method consists in heating a mixture of 107 kilos. of *p*-toluidine, 100 kilos. of naphthalene, and 60 kilos. of sulphur slowly to 180°, the temperature being then gradually raised to 210°. Hydrogen sulphide is uniformly evolved. The reaction is finished when no more free toluidine can be detected. The mixture is cooled and boiled with 30–40 per cent. sulphuric acid, in which the dehydro-compound is readily soluble. On cooling the solution, a solid layer separates on the surface, consisting of naphthalene and a small amount of impurities. The naphthalene, after being used several times, is purified by distillation.

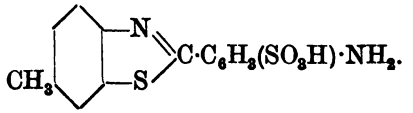
To isolate the base, the sulphuric acid solution is diluted strongly with water and neutralised with sodium carbonate. About 70 per cent. of the product consists of dehydrothio-*p*-toluidine (Cassella & Co., G.P., 53938).

Paul (*Zeitsch. angew. Chem.*, 1896, **9**, 681), who repeated this process with 2 kilos. of *p*-toluidine, obtained a 50 per cent. yield of dehydrothio-*p*-toluidine.

Dehydrothio-*p*-toluidine is insoluble in water, sparingly soluble in cold alcohol, but readily so in hot alcohol or amyl alcohol. It melts at 191° and boils at 434°.

It is used for making Diamine rose, Geranine, Erika 2GN, etc.

DEHYDROTHIO-*p*-TOLUIDINESULPHONIC ACID,



This is usually prepared by sulphonating the mixture of dehydrothio-*p*-toluidine and primuline base obtained in the "primuline melt," and separating the sulphonic acids by means of their ammonium salts.

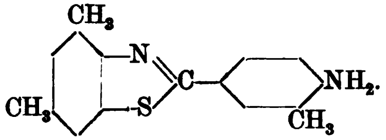
The "primuline melt" is made in an enamelled iron pot of about 200 gallons capacity which is set in brickwork and provided with an enamelled iron agitator. The lid of the pot also carries a thermometer tube, and a hole for charging and emptying which is closed by a flange. Connected with the lid is a cast iron pipe (preferably enamelled) of 8–10 in. internal diameter and about 40–50 ft. long. This pipe is inclined upwards at an angle, and serves as an air cooler to condense and return to the pot the *p*-toluidine which is carried off as vapour by the current of hydrogen sulphide. The whole or a part of the pipe can, if necessary, be cooled by a spray of water. From the further end a smaller pipe (2 in. diam.) carries the gas, which should then be quite cold, to an iron box, in which a little *p*-toluidine collects, and thence it passes to the furnace, where it is burnt under the pot, which it serves to heat, the excess being led away by a branch pipe to be burnt in the chimney. The pot is charged with 1,000 lb. of *p*-toluidine and 670 lb. of sulphur. This is heated to the boiling point for several hours, the temperature slowly rising as the reaction proceeds. The evolution of hydrogen sulphide commences at 170° and is completed when the temperature reaches 270°. The agitator is then stopped and the hot fluid is transferred from the pot under air pressure by means of a pipe inserted through the charging hole. After cooling and solidifying, the product is reduced to powder by means of a disintegrator. The yield is about 1,125 lb.

The sulphonation is performed in an enamelled iron-jacketed pan of 220 gallons capacity provided with cooling pipes through which cold water can be circulated. The contents of the pan can be rapidly stirred by means of an agitator, the blades of which pass between the loops of the cooling pipes. The ground melt (400 lb.) is dissolved with rapid agitation in 1,000 lb. of 100 per cent. sulphuric acid (final temperature about 90°). There is then added slowly, while the mixture is kept rapidly agitated and well cooled, 800–900 lb. of fuming sulphuric acid (containing 70 per cent. of sulphur trioxide). The temperature is not allowed to rise above 40°, and the operation lasts about six hours. (The same result is not obtained by initially employing, for example, 1,860 lb. of fuming sulphuric acid containing 32 per cent. of sulphur trioxide.) The sulphonation is complete when a small sample precipitated in water dissolves to a perfectly clear solution in boiling dilute ammonia. The mixture is then blown out of the pot by compressed air through the hollow spindle of the agitator, and is run by means of a lead pipe into a wooden vat containing about 3,000 gallons of cold water in which the dehydrothiotoluidine- and primuline-sulphonic acids are thrown down as a voluminous orange-yellow precipitate. This is filtered off through a wooden filter press, in which it is thoroughly washed with water until all mineral acid is removed. In order to effect the separation of the dehydrothiotoluidinesulphonic acid from the primulinesulphonic acid, the sparing solubility of the ammonium salt of the former is made use of. The mixed sulphonic acids, in the form of the wet press cake, are stirred up with cold concentrated ammonia in a wrought iron vessel provided with an agitator. The primuline dissolves whilst the ammonium dehydrothiotoluidinesulphonate separates out as a silky, crystalline precipitate. The mixture is transferred to a suction filter and the precipitate washed with a little water until nearly white. On adding common salt to the filtrate, the primuline is thrown down as a dark yellow, granular precipitate, which, after drying, is ground with sufficient common salt to bring it to standard strength. A small quantity which remains in the filtrate is recovered by adding the latter to the acid precipitating vat. The yield under the best conditions amounts to 530–560 lb. of ammonium dehydrothiotoluidinesulphonate, and 1,700–1,800 lb. of standard primuline, from 1,000 lb. of *p*-toluidine (Green, "Dictionary of Applied Chemistry," Thorpe, 1913, IV., 386, where the plant is figured).

Dehydrothio-*p*-toluidinesulphonic acid crystallises in yellow needles ($+H_2O$) or orange leaflets ($+2H_2O$) insoluble in water. The ammonium salt crystallises with $1H_2O$ and is sparingly soluble.

It is used for making Alkali brown, Rosophenine 10B, Clayton yellow (Thiazole yellow), Oriol yellow, Dianil yellow, Nitrophenine, Oxyphenine (Direct fast yellow, Columbia yellow, Diamine fast yellows), Chlorophenine, and Diphenyl fast yellow.

DEHYDROTHIO-*m*-XYLIDINE,

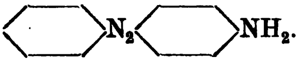


This base is prepared by heating *m*-xylidine (6 parts) with sulphur (1 part) to the boiling point until evolution of hydrogen sulphide ceases (for details, see p. 78). After removal of the excess of *m*-xylidine by distillation, it is separated from *iso*dehydrothio-*m*-xylidine (m. p. 121°), formed simultaneously, by means of 30 per cent. hydrochloric acid in which the *iso*-base is insoluble (Anschütz and Schultz, *Ber.*, 1889, **22**, 582; Paul, *Zeitsch. angew. Chem.*, 1896, **9**, 679).

Dehydrothio-*m*-xylidine melts at 107° and boils at 283°/14 mm. It is insoluble in water, very readily soluble in hot alcohol, but sparingly so in cold.

It is used for making Salmon red, Erica BN and 2GN.

AMINOAZOBENZENE,



Descriptions of the manufacture of this azo-compound have been given by Dale and Caro (E.P., 3307 of 1863), Graessler (E.P., 43 of 1879; F.P., 128113; G.P., 4186) and by Städel and Bauer (*Ber.*, 1886, **19**, 1953). Two more modern processes are given by Paul (*Zeitsch. angew. Chem.*, 1896, **9**, 689) and Jansen (*Zeitsch. Farb. Ind.*, 1913, **12**, 197).

Paul's method is as follows: 464 kilos. of aniline are placed in a tub (1,000 litres capacity) fitted with a lid carrying a flue, and a stirrer, and 640 kilos. of hydrochloric acid (20° Bé.) are run in. The temperature rises to about 75°, and the mixture is stirred for several days to cool, the crusts of aniline hydrochloride being detached from the sides of the tub at intervals.

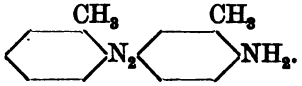
27·6 Kilos. of this mixture are placed in a cask, the temperature reduced to 8–10° by adding ice, and then 13·8 kilos. of a 25 per cent. solution of sodium nitrite are added with stirring, the temperature being kept below 10°. The diazoaminobenzene so formed is transferred to a tub, and the operation is repeated ten to fifteen times in the day. The whole of the diazoaminobenzene is kept stirred, and the temperature rises to 30–40° and should be kept at this point by the use either of ice or steam. The molecular change is complete when a sample added to alcohol and dissolved by a few drops of ammonia gives no further red colour on adding a few drops of sodium hydroxide solution. The batch is now filtered in a filter press fitted with woollen cloths, the cake of aminoazobenzene hydrochloride is stirred again in the tub with water and a few kilos. of hydrochloric acid, filtered, and this process repeated once or twice or until the substance is free from aniline. The yield is 173 kilos. of 44 per cent. paste or 76 kilos. of the dry hydrochloride from 10 × 11·6 = 116 kilos. of aniline, 16 kilos. of hydrochloric acid, and 3·6 kilos. of sodium nitrite, these quantities being in the molecular ratio of 2·5 : 2·5 : 1. Forty-two kilos. of aniline are recovered.

The product is a bright steel-blue, crystalline mass. It is tested by stirring with alcohol, boiling with ammonia, filtering, and precipitating the solution with sulphuric acid, the precipitated sulphate being dried and weighed. The yield is 75 per cent. of the theoretical.

Jansen's Process.—The operation is carried out in a lead-lined iron pan fitted with a jacket for water-cooling, and a lead-covered or enamelled stirrer. The lid is also lead-lined and carries a thermometer, and a blow-out pipe can be fitted to it. Thirty-nine litres of water and 54 kilos. of sodium nitrite are stirred until the latter is dissolved, 558 kilos. of aniline are added, and then, at 25–30°, 88 litres of hydrochloric acid are run in slowly, with stirring, during three to four hours. The temperature is then allowed to rise to 35° and is maintained at that point until the change from diazoaminobenzene to aminoazobenzene is complete. After five to six hours a sample is dissolved in excess of acetic acid and a drop of the solution is brought into contact on filter paper with a drop of an acetic acid solution of α-naphthylamine. If diazobenzene is present, a violet rim will be produced after a few seconds. Stirring is continued at 35° until this reaction is not obtained. To remove the excess of aniline, the whole is neutralised with hydrochloric acid and the aminoazobenzene hydrochloride, which separates in small, ruby-red crystals, is filtered from the solution of aniline hydrochloride and washed with dilute hydrochloric acid on the filter.

Aminoazobenzene melts at 127° and is used for making Fast yellow, Oil red O, Cloth red G, Croceines, Brilliant croceine M, Ponceau 5R, Azo acid violets, and Indulines.

o-AMINOAZOTOLUENE,



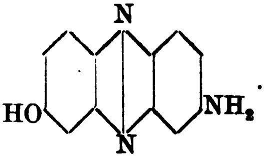
This may be prepared by Jansen's method of making aminoazobenzene (p. 81), substituting *o*-toluidine for aniline.

Alternatively, 85 lb. of *o*-toluidine are mixed with 24 lb. of solid sodium nitrite in an enamelled pan fitted with a stirrer and set in a water-bath. Then 50 lb. of concentrated hydrochloric acid are run in very slowly (five to six hours), the temperature being kept at 25° until towards the end, when it is allowed to rise to 30–35°, but must not exceed 40°. Next day the mass is heated to 60–70° until it is liquid, and then 60 lb. of concentrated hydrochloric acid are added quickly, the whole being well stirred during this operation. The mixture is cooled by means of the water-bath, diluted with water, filtered on an open filter of woollen cloth, and washed with acidified water. The crystalline paste of hydrochloride is then used directly for the preparation of azo-dyes. The hydrochloride is sparingly soluble in water, but more readily so in alcohol.

The base is very sparingly soluble in water, readily so in alcohol or ether, and melts at 100°.

It is used for making Cloth reds and Safranine and is also sold as Yellow fat colour and as Fast azo garnet base.

3-AMINO-7-HYDROXYPHENAZINE,



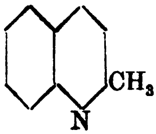
The preparation of this compound is described by Nietzki and Simon (*Ber.*, 1895, **28**, 2974) as follows: Ten grams of 2 : 4-diamino-4′-hydroxydiphenylamine hydrochloride (prepared by reducing the corresponding dinitro-derivative with stannous chloride and hydrochloric acid, with iron and acetic acid or with sodium hyposulphite) are dissolved in 300 grams of water and 10 c.c. of ammonia, 10 grams of manganese dioxide paste (60 per cent. "Weldon mud") are added, and the mixture is heated on the water-bath until the blue colour has disappeared, a drop placed on filter paper showing no blue rim. The whole is filtered hot, the residue boiled with water, and the filtrate acidified with hydrochloric acid, when, on cooling, the hydrochloride of the phenazine separates in brown needles. The yield is about 50 per cent. of the theoretical. The hydrochloride may be purified by recrystallisation from dilute hydrochloric acid. The base is obtained from the hydrochloride by the action of sodium carbonate.

According to Ullmann and Gnaedinger (*Ber.*, 1912, **45**, 3442), air is blown for four hours through a solution of 8·24 grams of *m*-phenylenediamine sulphate, and 6 grams of *p*-aminophenol hydrochloride in 5 litres of water after adding 5·2 grams of sodium hydroxide. A 70 per cent. yield of the compound $NH{:}C_6H_3(NH_2){:}N{\cdot}C_6H_4{\cdot}OH,2H_2O$ (m.p. 133°) is obtained and 4 grams are dissolved in 30 c.c. of 24 per cent. ammonia, the solution is diluted with water to 400 c.c., warmed on the water-bath and air blown in until the blue colour changes to red. The hydrochloride of the phenazine is precipitated from the filtered solution by means of hydrochloric acid. The yield of base from this is 2·4 grams, or 70 per cent. of the theoretical.

3-Amino-7-hydroxyphenazine sinters at 358° and melts above 360°; it dissolves in alcohol or ether with a green fluorescence. It is also soluble in alkali hydroxide.

It is used for making Immedial maroon B.

QUINALDINE,
(2-METHYLQUINOLINE)



Eight kilos. of aniline hydrochloride are dissolved in 16 litres of water, the solution is cooled with ice, and a cooled dilute solution of 5 kilos. of acetaldehyde (or paracetaldehyde) is added, the mixture being kept ice-cold. The condensation is complete in three to four days. On evaporation of the solution, the hydrochloride of a base, $C_{18}H_{20}N_2$, is obtained as a readily soluble, brownish-red mass; the base can be obtained from the solution by treatment with alkali, and separates in white flocks (Aktiengesellschaft für Anilinfabrikation, E.P., 4207 of 1883; G.P., 28217).

Five hundred grams of the above base are dissolved in 370 grams of hydrochloric acid (the above solution can obviously be used), a solution of 250 grams of zinc chloride is added, and the whole evaporated to dryness. The residue is now melted in a closed iron pan fitted with a stirrer and condenser. Water is given off, and at 130–140° the mass becomes so viscous that it can no longer be stirred. On further heating, however, it becomes fluid again and an oil distils with the water. At 180–200° much frothing occurs, and the mass must be rapidly stirred to prevent the material from foaming over. The temperature is finally raised to 280° and kept at this point for a short time. On cooling, the product is dissolved in water, the solution rendered alkaline, and the oil which separates is driven over with steam. The quinaldine passes over slowly (with 100 parts of water) and the oil, after being separated from water, is fractionally distilled, when the chief amount (about 175 grams) passes over at 238–258° (Schultz, *Ber.*, 1883, **16**, 2600; "Die Chemie des Steinkohlentheers," 1900, I., p. 119). A specimen of commercial quinaldine from the Aktiengesellschaft für Anilinfabrikation, and presumably made by the above process, was found to contain 14–16 per cent. of tetrahydroquinaldine (Jones and Evans, *Trans.*, 1911, **99**, 339).

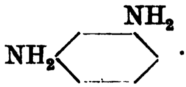
Another process consists in boiling a mixture of aniline (100 parts), paracetaldehyde (150 parts), hydrochloric acid (200 parts), and aluminium or zinc chloride (5 parts) for four to five hours (Chemische Fabrik auf Aktien vorm. Schering, E.P., 956 of 1883; F.P., 153873; G.P., 24317), but this gives a poorer yield than the one described above.

Quinaldine has also been synthesised from *o*-nitrophenyl hydroxyethyl methyl ketone (Heller and Sourlis, *Ber.*, 1908, **41**, 2692).

Quinaldine is a colourless oil which boils at 246–247°. It is used for making Quinoline yellow.

Diamino-compounds and their Derivatives.

m-Phenylenediamine,



This is manufactured by reducing *m*-dinitrobenzene with iron and hydrochloric acid in a reduction pan such as is used for the reduction of nitrobenzene. The following recipe is given by Harmsen ("Die Fabrikation der Theerfarbstoffe und ihrer Rohmaterialien," 1889, p. 81). Two hundred kilos. of dinitrobenzene and 200 litres of water are heated to the boiling point by direct steam in a reduction pan, 16 kilos. of hydrochloric acid are added, and then 420–450 kilos. of ground iron borings. The iron is added gradually, but extreme care must be taken that the reaction does not stop, as, should this occur, it may start again with almost explosive violence. This may be avoided by seeing that the reflux condenser is constantly acting. The reaction is at an end when a drop of the liquid, brought on filter paper, is no longer yellow. Sodium carbonate is now added until an alkaline reaction is obtained, 800–1,000 litres of water are run in, and the whole is boiled and then filtered through a filter press. The iron residue is boiled out again with 1,000 litres of water and filtered. The latter wash-water can be used for diluting the next batch. The filtrate containing the *m*-phenylenediamine is usually employed direct for making dyes. If a solid product is required, the filtrate is evaporated in a lead-lined pan and the hydrochloride precipitated by adding hydrochloric acid. It is then·centrifuged and dried.

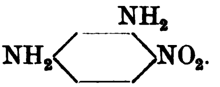
Grandmougin (*Rev. prod. chim.*, 1917, **20**, 260) gives different relative quantities for the above operation, namely, 200 kilos. of *m*-dinitrobenzene, 300 litres of water, 16 kilos. of hydrochloric acid, and 200–250 kilos. of iron borings.

To obtain the free base, Grandmougin (*loc. cit.*) recommends reducing 350 parts of dinitrobenzene as before, but using 50 parts of acetic acid (50 per cent.) and 700 parts of iron. The water and acetic acid are distilled off at the end of the reaction, and the residual *m*-phenylenediamine is then distilled in a vacuum.

In order to prepare the hydrochloride, Pomeranz (G.P., 269542) suspends 100 parts of *m*-dinitrobenzene in 1,300 parts of hydrochloric acid (19° Bé.) and introduces iron turnings at 40–50°. The liquid boils owing to the vigorous reaction and the iron is added so as to keep up this reaction, but of course not so quickly as to cause the liquid to boil over. When all the iron (250 parts) is dissolved, the solution is allowed to cool and *m*-phenylenediamine hydrochloride crystallises out and is filtered off. The product is quite white and the yield 95 per cent. of the theoretical. The operation, however, has to be conducted in earthenware and a large amount of ferrous chloride is produced.

m-Phenylenediamine melts at 61°, boils at 282–284°, and is readily soluble in water. It is used for making Vesuvine (Bismarck brown, Manchester brown), Chrysoidine, and many azo-dyes.

NITRO-*m*-PHENYLENEDIAMINE,



$\mathrm{NH_2}\overset{\mathrm{NH_2}}{\langle\quad\rangle}\mathrm{NO_2}$.

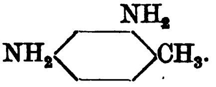
Five kilos. of 4-nitroaniline-3-sulphonic acid are heated with 20 kilos. of ammonia (25 per cent.) in an autoclave for three hours at 170–180°. On cooling, most of the nitro-*m*-phenylenediamine crystallises out and is filtered off. The reaction proceeds at 125°, but requires a longer time at this temperature (Aktiengesellschaft für Anilinfabrikation, F.P., 314468; G.P., 130438).

It can also be obtained by nitrating the diacetyl derivative of *m*-phenylenediamine and subsequent hydrolysis (Barbaglia, *Ber.*, 1874, 7, 1257).

Nitro-*m*-phenylenediamine melts at 161° and dissolves in water, alcohol, or ether.

It is used for making Pyramine orange R.

m-TOLYLENEDIAMINE,

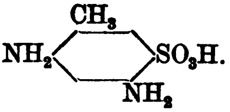


$\mathrm{NH_2}\overset{\mathrm{NH_2}}{\langle\quad\rangle}\mathrm{CH_3}$.

This is prepared from *m*-dinitrotoluene exactly as *m*-phenylenediamine is obtained from *m*-dinitrobenzene (p. 85).

It melts at 99°, boils at 280°, and is readily soluble in water. It is employed for the same purposes as *m*-phenylenediamine, and also for making Immedial yellow D, Immedial orange C, Cryogen yellows, etc.

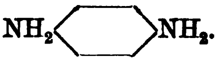
m-Tolylenediaminesulphonic Acid,



m-Tolylenediamine sulphate is added to the calculated quantity of fuming sulphuric acid and the mixture heated for three hours on the water-bath. On cooling, it is poured on ice, when the sulphate of the acid separates out. This may be converted into the hydrochloride and the solution used direct (Bückel, *Zeitsch. Farb. Ind.*, 1904, **3**, 137; Wiesinger, *Ber.*, 1874, **7**, 464; Oehler, F.P., 199658; G.P., 51662). The acid was also obtained by Foth (*Annalen*, 1885, **230**, 309) by sulphonating 2-nitro-*p*-toluidine ($CH_3 : NO_2 : NH_2 = 1:2:4$) with chlorosulphonic acid and reducing the product with stannous chloride.

It is used for making Toluylene orange R and G (Direct orange R and G, Oxydiamine orange R and G).

p-Phenylenediamine,



This is prepared by reducing aminoazobenzene or *p*-nitroaniline, the former being probably the cheaper method. The preparation is described by Jansen (*Zeitsch. Farb. Ind.*, 1913, **12**, 197).

From Aminoazobenzene.—The mixture of aminoazobenzene and aniline obtained in Jansen's method of preparation (p. 81) is not separated, but the contents of the lead-lined pan are blown into a cast iron reduction pan such as is used for the manufacture of aniline, except that a steam jacket surrounds its lower half. The pan is previously charged with 100 kilos. of ground iron borings, some water, and about 3 litres of hydrochloric acid (28 per cent.), and the mixture well stirred. Reduction begins as soon as the aminoazobenzene comes in contact with the iron and the temperature rises gradually to 30–40°. Stirring is continued overnight, and next morning the contents will have become completely colourless. The batch is now heated by means of the steam jacket, and steam is also blown through the hollow stirrer and the excess of aniline distilled off. The solution in the pan is allowed to settle, the clear solution pumped through the filter press, and the iron sludge washed out with hot water. The solution so obtained contains on the average 75 kilos. of *p*-phenylenediamine, which is about 85 per cent. of the theoretical quantity reckoned from the sodium nitrite used.

From p-*Nitroaniline.*—In this case no condenser is required to be fitted to the reduction pan, but the latter must have a flue fitted to the lid through which the steam may escape. Also no steam jacket is required. A large funnel, closed with a wooden plug, as for aniline, is fitted on the lid, above which is also a water tap. The pan is charged with 200 kilos. of ground iron borings, water, and 9 litres of hydrochloric acid (28 per cent.), so that the bottom wing of the agitator is just covered, and the mixture is boiled. Steam is then shut off and 200 kilos. of *p*-nitroaniline are added slowly, each addition being made after the cessation of the vigorous reaction caused by the previous one. Care must be taken that the mixture is not caused to boil over through too quick addition. Should this tend to occur, it may be corrected by adding cold water from the tap above the pan. It is necessary indeed, to allow a slow stream of water to flow into the pan to make up for the water lost as steam. When all the *p*-nitroaniline is in, the liquid is yellow; 14 litres of hydrochloric acid (28 per cent.) are added and stirring is continued. No vigorous reaction takes place, but the yellow colour soon vanishes. When a drop of the liquid, placed on filter paper, gives a colourless rim, the reduction is finished. Twenty-five kilos. of sodium carbonate are now added slowly, so that the solution has a faintly alkaline reaction to phenolphthalein, and the batch is boiled for ten minutes and allowed to settle. The clear, hot liquid is pumped through the filter press and the iron sludge washed out with hot water. The solution is evaporated until the base crystallises out on cooling. The yield is 90–95 per cent. of the theoretical, and the product is of a high degree of purity. If necessary, it can be distilled in a vacuum.

The following process of reducing aminoazobenzene is given by Ristenpart (" Organische Farbstoffe," 1911, p. 15). Sixty-seven kilos. of moist aminoazobenzene hydrochloride (70 per cent.) are suspended in 130 litres of water and 20 litres of alcohol and 35 kilos. of zinc dust are stirred in at such a rate as to keep the temperature between 60° and 70°. Towards the end, the temperature is raised to 90°, 15 kilos. of sodium carbonate are added, and the aniline (about 15 kilos.) distilled off by means of steam. The residue is filtered and the filtrate evaporated to a bulk of 65 litres. On cooling, 25 kilos. of *p*-phenylenediamine crystallise out.

It is stated (Aktiengesellschaft für Anilinfabrikation, E.P., 3875 of 1908; F.P., 397443; G.P., 202170) that *p*-phenylenediamine can be obtained by heating *p*-dichlorobenzene (150 parts) with ammonia (750 parts of 25 per cent.) and copper sulphate (20 parts) for twenty hours at 170–180°. The excess of ammonia is distilled off and the *p*-phenylenediamine obtained in the form of sulphate or hydrochloride.

Another method of preparing *p*-phenylenediamine consists in reducing *p*-nitroaniline with hydrogen, using reduced nickel as catalyst, in amyl-alcoholic solution. The reaction is carried out at 120–130° under a pressure of 10–15 kilos. per sq. cm. (Brochet, E.P., 16936 of 1913 ; F.P., 458033 ; U.S.P., 1247629).

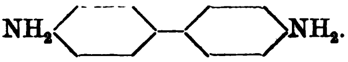
p-Phenylenediamine melts at 147° and boils at 267°, or 150°/13 mm. It is used for dyeing hair and for the manufacture of sulphide dyes and Safranine. In the latter case, the mixture obtained by reducing aminoazobenzene (without the presence of aniline as above) is employed direct.

ACETYL-*p*-PHENYLENEDIAMINE, (*p*-AMINOACETANILIDE)

p-Nitroacetanilide (p. 53), prepared from 10 parts of acetanilide, is mixed with about 100 parts of water and reduced in an open reduction pan with 12 parts of ground iron borings and 5 parts of acetic acid (40 per cent.) at a temperature not exceeding 60°. When the reduction is finished, the whole is rendered slightly alkaline with 3½ parts of sodium carbonate dissolved in 15 parts of water, filtered hot, and to the filtrate (which occupies a volume of about 150 parts of water) 15 parts of salt and 7½ parts of hydrochloric acid (19° Bé.) are added. The hydrochloride of acetyl-*p*-phenylenediamine crystallises out and is collected and dried. The yield is about 11 parts of the hydrochloride (Grandmougin, *Rev. prod. chim.*, 1917, **20**, 260). It is often not necessary to isolate the hydrochloride, in which case the filtrate is simply neutralised with hydrochloric acid so as to form the hydrochloride, and care is taken that sufficient water is present to prevent the salt crystallising out on cooling. The solution may then be used direct for preparing azo-dyes.

Acetyl-*p*-phenylenediamine melts at 162–162·5°, and is used for making Lanafuchsines (Sorbine reds), Amidonaphthol red 6B, Chromotrope 6B, Columbia blacks, etc.

BENZIDINE,



This is prepared by reducing nitrobenzene to hydrazobenzene in alkaline solution with zinc dust and transforming the hydrazobenzene to benzidine by means of hydrochloric acid.

Before describing the large scale manufacture, an account of some smaller experiments may be given.

Teichmann (*Zeitsch. angew. Chem.*, 1893, **6**, 67) gives the following recipe. A mixture of 100 grams of nitrobenzene, 80 grams of sodium hydroxide solution (D 1·4), and 500 c.c. of water is heated in a reflux apparatus on the water-bath; 160 grams of zinc dust are introduced in small portions, and during the addition, which extends over six to eight hours, the mixture is agitated. When cold, the product is gradually poured into 1,500 c.c. of hydrochloric acid (D 1·2), the temperature being kept low by the addition of ice. After this, the liquid is heated to boiling by passing in steam and is filtered from resinous matter while hot. The hot filtrate is then treated with a saturated solution of sodium sulphate, whereby almost the whole of the benzidine is precipitated as sulphate. It is collected, washed with water, and dried. The yield is 90 per cent. of the weight of nitrobenzene employed, and the product contains 2·5 per cent. of ash (this corresponds with 57·2 grams of benzidine).

Experiments on rather a larger scale were made by Erdmann (*Zeitsch. angew. Chem.*, 1893, **6**, 163).

A mixture of 2 kilos. of nitrobenzene, 6 litres of sodium hydroxide solution (40° Bé.), 2 litres of water, and 1 litre of alcohol is introduced into an earthenware cylinder furnished with a side tube and a lid having a hole to admit an iron or wooden mixer. The alcohol is not absolutely necessary, but the reaction proceeds with greater regularity when it is used, and less aniline is formed. The side tube is attached to a condenser and 3·4 kilos. of zinc dust are introduced in small portions through a tube fixed in the lid. An energetic action soon sets in, and a mixture of alcohol and nitrobenzene distils over, which is repeatedly returned. The addition of zinc dust is so regulated that the mixture does not froth over, and it is kept in agitation with the mixer; when these precautions are neglected, the reaction may become sufficiently violent to cause explosion; the reduction is complete in 2½ hours. The product is allowed to cool and, on the following day, diluted with water and thrown on a sieve, which allows the zinc oxide to pass through, but retains the crystals of hydrazobenzene; the hydrazobenzene may also be isolated by dissolving the zinc oxide at 10–15° in 18 litres of concentrated hydrochloric acid. The yield is 1,170 grams of hydrazobenzene, 128 grams of benzidine, and 18 grams of aniline. To convert the hydrazobenzene into benzidine, 500 grams of the former are boiled with 800 c.c. of concentrated hydrochloric acid and 1 litre of water; the precipitated benzidine hydrochloride is collected, and dilute sulphuric acid added to the filtrate as long as a precipitate falls, which is collected. The diphenyline contained in the filtrate represents 8–10 per cent. of the hydrazobenzene employed. The yield of benzidine does not exceed 50 per cent. of the weight of nitrobenzene reduced.

With regard to the transformation of hydrazobenzene into benzidine, a considerable amount of work has been carried out by van Loon (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, **5**, 377; **6**, 262 [with Holleman]; *Rec. trav. chim.*, 1904, **23**, 62), who found that, at the ordinary temperature, *N*/10-hydrochloric acid converts 84 per cent. of the hydrazobenzene into benzidine whilst normal hydrochloric acid converts 90 per cent. At 100°, *N*/10-hydrochloric acid transforms only 66·4 per cent. of the hydrazobenzene into benzidine.

The manufacture of benzidine is described by Schultz ("Die Chemie des Steinkohlentheers," 1900, I., p. 93) as follows: The reduction of nitrobenzene to hydrazobenzene by means of zinc dust and sodium hydroxide proceeds best in the presence of alcohol. Comparatively little sodium hydroxide is used, so that the reduction is carried on by zinc dust in the presence of sodium zincate.

The quantity of zinc dust to be used depends on its quality. Coarser particles are only slightly acted on and become embedded in the hydrazobenzene. The apparatus consists of a jacketed iron pan fitted with a stirrer, reflux condenser, steam pipe, manhole, and run-out pipe. This is charged with 100 kilos. of nitrobenzene and 50 kilos. of alcohol, the mixture is heated to the boiling point of the alcohol, and 150–160 kilos. of zinc dust are added. A mixture of 100 kilos. of alcohol and 13 kilos. of sodium hydroxide solution (36° Bé.) is now added during three to four hours, the liquid being kept gently boiling. When all is in, the mixture is stirred for half an hour longer and a sample taken. If this is not grey, 20 kilos. of water are added and the whole is heated to boiling; if necessary, more zinc is added until the reduction is complete.

The contents of the pan are now diluted with water and the alcohol is distilled over with steam. The residue is thrown on a fine sieve, which retains the hydrazobenzene and allows the zinc dust, zinc oxide, etc., to pass through; the hydrazobenzene is well washed with water. Alternatively, the whole batch can be diluted with water, cooled with ice, carefully neutralised with hydrochloric acid, and the hydrazobenzene filtered off.

The transformation of the hydrazobenzene is effected by treating it gradually with hydrochloric acid so that free acid is always present, the temperature being kept at 35°, and finally the mixture heated to boiling. It is filtered from dirt arising from the zinc dust, and the filtrate is precipitated with sulphuric acid or sodium sulphate. This is filtered, washed from all zinc salts, and the base liberated by boiling the sulphate with dilute sodium hydroxide solution ; on cooling, the benzidine is filtered off and can be purified by distillation in a vacuum.

The description of the manufacture given by Grandmougin (*Rev. prod. chim.*, 1917, **20**, 260) differs a little from the above. To the same quantities of nitrobenzene and alcohol he adds a mixture of 100 kilos. of alcohol and 40 kilos. of sodium hydroxide (36-40° Bé.) during five to six hours. The reaction is regulated by the rate of addition of the alkali and also, if necessary, by cooling. The contents of the pan are poured into 1,500 litres of sulphuric acid (20 per cent.), heated to boiling, and allowed to cool, when the benzidine sulphate is filtered off. The yield of sulphate ($C_{12}H_{12}N_2,H_2SO_4$) is 95 per cent. of the weight of the nitrobenzene, or 62 per cent. of the base, which is equivalent to 80–85 per cent. of the theoretical.

It seems likely that electrolytically deposited spongy zinc (Chemische Fabrik Griesheim-Elektron, G.P., 282234, 288413) would be more suitable than zinc dust in this reduction.

The use of alcohol, too, can be avoided if a very energetic stirrer is employed (Harmsen, " Die Fabrikation der Theerfarbstoffe," p. 264), or solvent naphtha may be substituted for it (G.P., 225245).

The zinc can be recovered either as chloride, by evaporating the hydrochloric acid solution, or as oxide, by precipitating the latter solution with lime.

Several other reducing agents have been suggested, but it would appear that zinc is the best. Thus, to obtain hydrazobenzene, the Chemische Fabriken vorm. Weiler-ter-Meer (E.P., 15706 of 1901 ; F.P., 314699 ; G.P., 138496 ; U.S.P., 691132) heats 1,000 kilos. of nitrobenzene with 1,250 kilos. of iron and 1,130 kilos. of sodium hydroxide (55° Bé.) gradually to 130°, or the reduction is carried only as far as the azobenzene stage (with 1,000 kilos. of iron and 830 kilos. of sodium hydroxide at 100–120°) and this extracted with benzene, the solvent evaporated, and the final stage of the reduction effected with zinc and sodium hydroxide.

Besides iron, other reducing agents recommended are the iron residues from the manufacture of aniline (G.P., 245081), iron pyrites or carbon (Farbenfabriken vorm. F. Bayer & Co., E.P., 15420 of 1907; F.P., 380175; G.P., 204653), molasses (G.P., 228722), sawdust (G.P., 225245), etc., but these processes are usually difficult to take past the azoxy- or azo-benzene stage.

A catalytic process for the hydrogenation of nitrobenzene in the presence of nickel and sodium hydroxide is described by Brochet (E.P., 22523 of 1913; First Addition, dated Oct. 8, 1912, to F.P., 458033).

The reduction of azobenzene by means of sulphur dioxide in the presence of potassium iodide is the subject of a patent by Bodenstein (G.P., 172569).

Much work has been done on the preparation of hydrazobenzene by electrolysis, but it is doubtful if this has yet passed the experimental stage.

An example may be given of Darmstädter's process (E.P., 6924 of 1906; G.P., 181116, 189312; U.S.P., 833513).

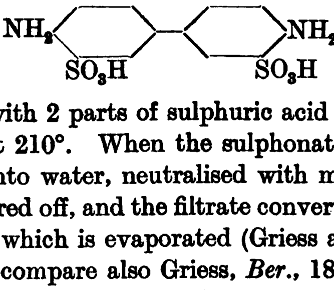
Nitrobenzene (100 grams) is suspended in 1 litre of 3 per cent. sodium hydroxide contained in the cathode cell; the anode liquid is 5–10 per cent. aqueous sodium hydroxide. The electrodes are preferably of iron or nickel, and 150–200 per cent. of the calculated current is sent through the cell with a current density of 2–3 amperes per sq. dcm. of cathode. The cathode solution is thoroughly agitated. In this way, the nitrobenzene is almost entirely reduced to hydrazobenzene, and the latter is separated from a small proportion of azoxybenzene by the action of hydrochloric acid, which transforms the hydrazo-compound into soluble benzidine hydrochloride (compare also E.P., 12596 of 1898; F.P., 278587; G.P., 100234; also G.P., 116467, 116871, 121899, 121900, 122046, 141535; Löb, *Ber.*, 1900, 33, 2329).

Hydrazobenzene melts at 127°.

Benzidine melts at 127·5–128° and boils at 400°. It dissolves in about 2,000 parts of water at the ordinary temperature and in about 90 parts of boiling water.

Benzidine is used for making Diamond Flavine G, Dutch yellow (Mordant yellow GRO), Pyramine orange 3G and 2R, Congo red, Diazo black B, Glycine red, Glycine Corinth, Orange TA, Congo Corinth G, Congo rubine, Congo orange G, Brilliant Congo G, Pyramidol brown BG, Benzidine puce, Diamine scarlet B, Bordeaux COV, Heliotrope 2B, Trisulphone violet B, Dianil blue R, Benzo violet, Chicago blue 4R, Columbia blue R, Oxamine violet, Diamine violet N, Diamine black BH, HW and RO, Diamine browns, Zambesi brown G, Alkali dark brown GV, Dianil garnet B (Benzo fast red 9BL), Diphenyl blue black, Diphenyl grey, Naphthamine black RE (Naphthylamine diazo black), Benzocyanine R, Diamine blue 2B, Naphthamine blue 2B, Wool red G, Brilliant orange G, Benzo orange R, Chlorazol orange 2R, Crumpsall direct fast red, Chrysamine G, Diamine fast red F, Oxamine maroon, Oxamine red, Diphenyl browns, Alkali yellow R, Cresotine yellow G, Direct violet R, Direct indigo blue, A, BN and BX, Direct grey R, Melogen blue BH, Diazo blue black RS, Direct black V, Direct indone blue R, Benzo olive, Benzo grey S extra, Diamine bronze G, Trisulphone brown B, Erie direct black GX and RX (Direct deep black EW and RW), Erie direct green ET, Columbia black green D, Eboli greens, Diphenyl green G and 3G, Chloramine black N, Chloramine green B, Chloramine blue 3G and HW, Diamine green B and G, Benzamine brown 3GO, Congo brown G and R, Columbia green, Dianil black R, Hessian brown BBN, and Cotton brown A and N.

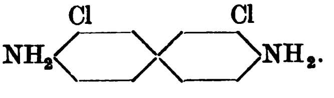
BENZIDINEDISULPHONIC ACID, (4 : 4′-DIAMINODIPHENYL-3 : 3′-DISULPHONIC ACID)



Benzidine sulphate is heated with 2 parts of sulphuric acid for thirty-six to forty-eight hours at 210°. When the sulphonation is finished, the mass is poured into water, neutralised with milk of lime, the calcium sulphate filtered off, and the filtrate converted into sodium salt, the solution of which is evaporated (Griess and Duisberg, *Ber.*, 1889, **22**, 2464; compare also Griess, *Ber.*, 1881, **14**, 300, and Farbenfabriken vorm. F. Bayer & Co., E.P., 1074 of 1884; G.P., 27954).

The acid is sparingly soluble in water. It is used for making Pyramine orange R.

3 : 3′-DICHLOROBENZIDINE,



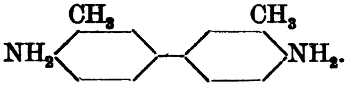
This is prepared by chlorinating diacetylbenzidine and subsequently hydrolysing the product, or by reducing *o*-chloronitrobenzene with zinc in alkaline solution. The latter method is to be preferred.

26·8 Kilos. of diacetylbenzidine (prepared by boiling benzidine with excess of glacial acetic acid and pouring into water) are dissolved in about 3 times the weight of sulphuric acid at the ordinary temperature, and the solution is poured into ice-water. A 10 per cent. solution of bleaching powder (or sodium hypochlorite solution), sufficient to form a dichloro-derivative, is added gradually, the temperature being kept low. The chlorination is finished when the green colour changes to a pale yellow. The temperature is now raised to 40° and kept at that point for twelve hours. The substance is filtered off and hydrolysed by boiling it with 3–4 times its quantity of 20 per cent. hydrochloric acid, when, on cooling, the greater part of the hydrochloride separates, from which the base is obtained in the usual way (Levinstein, E.P., 25725 of 1896; F.P. 265155; G.P., 94410; U.S.P., 625174).

The base is prepared from *o*-chloronitrobenzene in the same way as benzidine is obtained from nitrobenzene. No large scale description of the process has been published, so reference should be made to the method of making benzidine on p. 91 (compare also Cohn, *Ber.*, 1900, **33**, 3551).

3 : 3′-Dichlorobenzidine melts at 133° and is used for making Dianol brilliant red extra (Diphenyl red 8B).

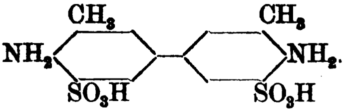
o-Tolidine,



This base is prepared exactly as benzidine (p. 91), except that the starting point is *o*-nitrotoluene.

Hydrazotoluene melts at 165°.

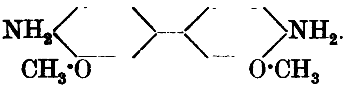
Tolidine melts at 129°, dissolves in 7,000 parts of cold, and 300 parts of hot, water, and is used for making Benzoyl rose, Naphthamine blue 3B, Toluylene orange G and R, Benzopurpurine B, 4B and 6B, Diamine red B and 3B, Deltapurpurine 5B and 7B, Brilliant purpurine 4B and R, Brilliant Congo R, Rosazurine B and G, Congo Orange R, Congo 4R, Congo Corinth B, Pyramidol brown T, Azo blue, Trisulphone blue R, Dianil blue B and 2R, Azo black blue B and R, Azo mauve B, Naphthazurine B, Chicago blue R and 2R, Oxamine blue 4R, Diamine blue BX and 3R, Columbia blue G, Eboli blues, Benzocyanine B, Diphenyl brown 3GN, Chrysamine R, Cresotine yellow R, Indazurine RM and TS, Direct blue R, Direct grey B, Benzo black blue R, Congo fast blue R, Benzo indigo blue, Columbia black R, Trisulphone brown G and Azo Corinth.

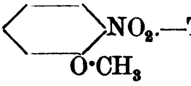
o-Tolidinedisulphonic acid, 

This is prepared from tolidine sulphate in the same manner as benzidinedisulphonic acid is obtained from benzidine sulphate (p. 92) (Griess and Duisberg, *Ber.*, 1889, **22**, 2464).

The acid is readily soluble in hot water and the disodium salt crystallises with $5H_2O$.

It is used for making Acid anthracene red 3B.

Dianisidine, 

Preparation of o-*Nitroanisole,* —This is prepared by two methods, namely, (1) by methylating *o*-nitrophenol, and (2) by the action of methyl alcohol and sodium hydroxide on *o*-chloronitrobenzene (newer method). Brand (*J. pr. Chem.*, 1903, [ii], **67**, 145) has described some experiments on the second method as follows: One hundred grams of *o*-chloronitrobenzene are dissolved in 200 c.c. of methyl alcohol and a solution of 40 grams of potassium hydroxide in 200 c.c. of water and 300 c.c. of methyl alcohol are added. The mixture is boiled under a reflux condenser for about twenty-six to thirty-one hours, and then the greater part of the alcohol is distilled off. Steam is now passed in and any unchanged *o*-chloronitrobenzene is driven over, together with some *o*-nitroanisole, in the first 20 grams of distillate. The rest of the distillate contains *o*-nitroanisole. The first distillate should be used again in the next experiment, as it is very difficult to separate the ingredients by fractional distillation.

The preparation of *o*-nitroanisole is described by Jansen (*Chem. Zeitsch.*, 1913, **12**, 171; *Zeitsch. Farb. Ind.*, 1913, **12**, 247) as follows:

Eighty-three kilos. of sodium hydroxide solution (37° Bé.), 180 litres of water, and 75·5 kilos. of *o*-nitrophenol are placed in a cast iron steam-jacketed pan and evaporated to a thick paste. On cooling, the whole sets to a hard cake (162 kilos.). One hundred and sixty kilos. of this are transferred to an autoclave fitted with a stirrer, and 60 kilos. of sodium carbonate (dry) and 90 kilos. of alcohol are added. The autoclave is shut and 51·5 kilos. of methyl chloride are led in. The stirrer is kept going slowly for about twelve hours. The autoclave is jacketed with sheet iron, which is protected by wood, and a thermometer is placed in the sheet iron casing. During the twelve hours' stirring, steam is blown into the casing until the thermometer shows 90–100°, whereby the autoclave is kept uniformly at a moderate temperature. Next day the pressure is released, the autoclave opened, and the contents are transferred to a distilling pan fitted with a stirrer. About 100 litres of water are added and the whole is distilled until water alone passes over. The residue is run into a reservoir half filled with hot water and left for a day. The water is then drawn off and the oil washed in a separator with dilute hydrochloric acid. Sixty kilos. of *o*-nitroanisole and 20 kilos. of salt residue are obtained, from which more oil can be extracted by distillation.

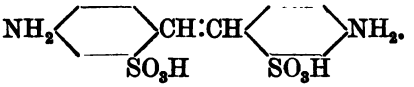
o-Nitroanisole melts at 9° and boils at 265°.

Reduction.—In a jacketed reduction pan fitted with stirrer and reflux condenser 30 kilos. of *o*-nitroanisole, 40 kilos. of zinc dust, and 20 kilos. of alcohol are heated by means of indirect steam. As soon as the reduction begins, 18 kilos. of alcoholic sodium hydroxide (14 kilos. of alcohol and 4 kilos. of sodium hydroxide solution of 37° Bé.) are run in slowly in a thin stream until the mass is pale grey. This operation takes about six hours. Then three buckets of water are added (60 lb.) and the whole is blown to a reservoir 1·25 metres high and 1 metre in diameter; 5 kilos. of hydrochloric acid, diluted with a little water, are added, and the whole is filled up to 45 cm. high with water. After settling, the mass is filtered through a woollen filter.

In a lead-lined tub (1·13 metres high and 1·25 metres in diameter) 18 cm. of water are run, and then 173 kilos. of sulphuric acid (free from arsenic). The tub has a cover and a wide outlet to it. When the acid mixture has cooled to 48–50° the hydrazoanisole is added, and the total liquid should be 39 cm. high. The mixture is stirred for five hours and then warmed to 60° during two hours, stirred two hours longer, then warmed to 90° and 2 kilos. of zinc dust are added, when the liquid becomes almost colourless. At the end it should be only yellowish, not brown. It is now filtered at 90° into a second tub and treated with 1 kilo. of sodium thiosulphate and 1 kilo. of hydrochloric acid, then 250 kilos. of hydrochloric acid are added, and the whole is stirred for a few hours. After two days the mass becomes thick and is filtered on a box filter through wool. The crystalline mass is stirred in a tub with ten buckets of hot water (200 lb.) and heated with direct steam until all is in solution. This is filtered through a wool filter and the residue boiled out again and filtered. To the total liquid, when boiling, 55 kilos. of ammonia are added all at once, the whole being well stirred. The tub is covered and left for two days. The base is then filtered, washed with dilute ammonia, and then with very dilute sodium hydroxide until the filtrate is alkaline to phenolphthalein. The yield is 20 kilos.

Dianisidine melts at 135° and is only sparingly soluble in water. It is used for making Benzopurpurine 10B, Diazurine B, Azo violet, Dianisidine blue, Trisulphone blue B, Benzoazurine G and 3G, Congo blue 2B, Direct violet 2B, Indazurine B, 2B, GM and 5GM, Dianil blue G, Brilliant azurine 5G, Diamine brilliant blue G, Chicago blue B, 4B, 6B and RW, Azidine wool blue B, Oxamine blue B, Benzocyanine 3B, Diamine sky blue, Direct blue B, Columbia black B, Congo fast blue B and Trisulphone brown GG.

DIAMINOSTILBENEDISULPHONIC ACID,



Fifty kilos. of sodium *p*-nitrotoluenesulphonate are dissolved in 700 litres of boiling water and digested with about 50 kilos. of 33 per cent. sodium hydroxide solution. When the colour has become deep red, zinc dust is added gradually until the liquid becomes decolorised. The whole is filtered and the diaminostilbenedisulphonic acid is precipitated with hydrochloric acid, filtered off, and washed. It can be purified by dissolving in sodium carbonate, filtering, and acidifying (Leonhardt & Co., E.P., 4387 of 1886; G.P., 38735; U.S.P., 360553.)

Bender and Schultz (*Ber.*, 1886, **19**, 3234) give quantities slightly different from the above, namely, 50 grams of sodium *p*-nitrotoluenesulphonate dissolved in hot water and 100 c.c. of 33 per cent. sodium hydroxide solution, 50 grams of zinc dust being subsequently added.

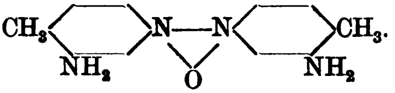
Another modification consists in adding 70 litres of sodium hydroxide solution (33 per cent.) to a boiling solution of 36 kilos. of sodium *p*-nitrotoluenesulphonate in 100 litres of water. After half an hour, 360 litres of water are added and then, gradually, 50 kilos. of zinc dust. The whole is boiled until the liquid no longer turns red on exposure to the air, when it is filtered into hydrochloric acid. About 13 kilos. of the diamino-acid are obtained (Ristenpart, " Organische Farbstoffe," 1911, p. 25).

The acid is also obtained by reducing dinitrostilbenedisulphonic acid, thus 100 lb. of the acid are dissolved in 100 gallons of boiling water with the addition of 50 gallons of hydrochloric acid. To the boiling solution 150 lb. of zinc dust are slowly added, and when the reduction is complete the precipitate is filtered off, extracted with sodium carbonate, filtered from undissolved zinc, and the diaminostilbenedisulphonic acid precipitated from the filtrate by acidifying with hydrochloric acid. (Green and Wahl, E.P., 5351 of 1897. Compare F.P., 269466; G.P., 98760.)

The acid is almost insoluble in water, but the salts are readily soluble.

It is used for making Hessian purple N, Hessian brilliant purple, Renol brilliant yellow (Paper yellow 3G), Chrysophenine G, and Hessian yellow.

p-AZOXY-*o*-TOLUIDINE,



This base is obtained by the alkaline reduction of *p*-nitro-*o*-toluidine. Noelting and Collin (*Ber.*, 1884, **17**, 261, 268) prepared *p*-nitro-*o*-toluidine by nitrating *o*-toluidine dissolved in 10 parts of sulphuric acid, and Green and Lawson (*Trans.*, 1891, **59**, 1013) showed that the product of nitration contained 75 per cent. of this compound, about 3–4 per cent. of 5-nitro-*o*-toluidine (m. p. 130°), and about 20 per cent. of 6-nitro-*o*-toluidine (m. p. 91·5°).

Limpricht (*Ber.*, 1885, **18**, 1400) obtained the compound by reducing *m*-dinitrotoluene with alcoholic ammonium sulphide, and prepared *p*-azoxy-*o*-toluidine from it by reduction with sodium amalgam. Green and Lawson found that sodium stannite was the most suitable reducing agent.

On the large scale, the reduction is effected by means of zinc dust and sodium hydroxide or by dextrose and sodium hydroxide.

Preparation of p-*Nitro*-o-*toluidine.*—The nitration of *o*-toluidine (Jansen, *Zeitsch. Farb. Ind.*, 1913, **12**, 181) is carried on in a cast iron pan of about 1,000 litres capacity fitted with a jacket and internal coils for cooling with water or salt solution at −10° from an ice machine. The pan is charged with 840 kilos. of sulphuric acid (98 per cent.), cooling water turned on, and 192 kilos. of *o*-toluidine, which must not contain more than 1 per cent. of *p*-toluidine, are added very slowly with good stirring, the temperature being allowed to rise to 30–35°. White lumps of the sulphate are formed on the surface, which, however, redissolve. When all is in solution, the cooling water is shut off and salt solution at −10° is circulated through the jacket and coils. As soon as the temperature has fallen to +10°, a mixture of 125 kilos. of nitric acid (90 per cent.) and 300 kilos. of sulphuric acid (98 per cent.) is allowed to flow into the solution by means of a funnel, the end of which dips underneath the surface of the liquid. The temperature must be kept at 10°, but towards the end it may rise to 12°. The concentration of the acids must be that given above, as otherwise the mass solidifies and cannot be blown out of the pan. The finished nitration mixture is blown into a tub of 6,000 litres capacity in which is contained 1,200 kilos. of sodium chloride dissolved to 4,500 litres. The sulphate of *p*-nitro-*o*-toluidine separates out as a pale yellow, crystalline mass, whilst the 6-nitro-*o*-toluidine remains in solution. The whole is stirred for twenty-four hours to complete the precipitation.

One hundred c.c. of the filtrate from a sample should not absorb more than 8 c.c. of normal sodium nitrite solution, which corresponds with about 55 kilos. of 6-nitro-*o*-toluidine. The precipitated sulphate is filtered on a vacuum filter and washed with small amounts of saturated salt solution. The yield of *p*-nitro-*o*-toluidine is about 190 kilos. reckoned as base.

p-Nitro-*o*-toluidine melts at 107°, boils at about 310°, and dissolves in 100 parts of boiling water. It is also used for making Pigment orange R.

*Azoxy-*o*-toluidine.* (1) *Reduction with Zinc Dust.*—To a boiling solution of 15·2 kilos. of *p*-nitro-*o*-toluidine in about 1,200 litres of water and 144 litres of sodium hydroxide solution (36° Bé.) are added 19 kilos. of zinc powder in small portions at a time. A yellow precipitate is formed, which is purified by crystallisation from water acidified with hydrochloric acid. Alternatively, the same weight of nitrotoluidine is boiled with 300 litres of water and 15 kilos. of zinc dust (88 per cent.) and 100 kilos. of sodium hydroxide solution (D 1·36) are added gradually within an hour, and the mixture is heated for eight to ten hours (Société Anonyme des Matières Colorantes et Produits Chimiques de St. Denis, E.P., 9315 of 1887; F.P., 184549; G.P., 44045; U.S.P., 380927).

(2) *Reduction with dextrose.*—Jansen (*loc. cit.*) gives the following details:

The reduction is effected in a tall pitch-pine tub with stirrer, of about 9,000 litres capacity. It is fitted with a removable iron steam pipe which reaches almost to the bottom, and two 2-inch taps (made of tombac, a brass containing 80 per cent. of copper), one at the bottom and the other about 35 cm. higher. A smaller tub (1,500 litres) is placed above this, which is fitted with a steam pipe and a tap at the bottom.

The steam pipe is removed from the larger tub and the paste of *p*-nitro-*o*-toluidine sulphate is put in with about 900 litres of water; the solution is stirred, and about 150–200 kilos. of sodium carbonate are added gradually to neutralise it. Two hundred and twenty-five litres of sodium hydroxide solution (30 per cent.) are now added, the steam pipe is fixed in position, and the mixture rapidly heated to about 95°, care being taken not to have more condensed steam present than is necessary.

The steam is now shut off and a solution of 285 kilos. of dextrose in about 900 litres of water, which has been previously prepared in the smaller tub, is added rapidly. A vigorous reaction sets in, and when this has subsided the whole is boiled for fifteen to twenty minutes to complete the reduction. The azoxytoluidine should form a brownish-yellow, crystalline powder, which settles rapidly to the bottom when the stirrer is stopped. The supernatant liquor should not be darkly coloured, as this indicates that the reduction has proceeded too far and some *m*-tolylenediamine has been formed. The tub is then filled up with cold water, stirred, and the product allowed to settle.

Next morning, the clear liquor is run off through the higher tap, the residue stirred and run on an open cotton filter, and washed with water until free from sodium hydroxide. In order to purify it, the base is stirred with about 2,500 litres of water in a tub of about 4,000 litres capacity, and hydrochloric acid (175–180 litres of 28 per cent.) added until it is just dissolved; an excess of acid must be avoided. A clear solution is obtained from which, by the gradual addition of 260 kilos. of salt, the hydrochloride of the base is precipitated as a grey, crystalline powder. A sample is filtered and sodium acetate added to the solution in order to see whether all the hydrochloride has been precipitated. If this is the case, the solid is filtered on an open cotton filter. The yield of pure base is equal to about 68–70 kilos. of sodium nitrite, that is, about 130 kilos. of base or 56 per cent. of the theoretical.

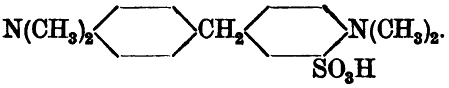
Azoxytoluidine melts at 168° and is used for making azo-dyes, chiefly Rouge de St. Denis (Rosophenine 4B).

4 : 4′-Tetramethyldiaminodiphenylmethane,

The following method of preparation is given by Möhlau and Heinze (*Ber.*, 1902, **35**, 359). Two hundred and fifty-four grams of dimethylaniline (corresponding with 2 mols. and an excess of 5 per cent.) are mixed with an equal weight of hydrochloric acid (D 1·19), and, after cooling, 75 grams (1 mol.) of formaldehyde (40 per cent.) are added.* The clear mixture is warmed on the water-bath for a day, and on the next day is again heated and rendered alkaline with sodium hydroxide. The excess of dimethylaniline is driven over with steam, and the oily layer of tetramethyldiaminodiphenylmethane crystallises on cooling. Practically a theoretical yield is obtained. The crude substance can be crystallised from alcohol.

4 : 4′-Tetramethyldiaminodiphenylmethane melts at 91°, boils at 390°, and is used for making tetramethyldiaminobenzhydrol and Auramine.

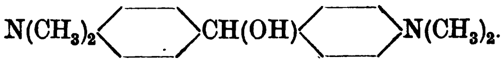
Tetramethyldiaminodiphenylmethanesulphonic Acid,



Twenty kilos. of tetramethyldiaminodiphenylmethane are heated with 20 kilos. of sulphuric acid (100 per cent.) to 110° in a lead-lined pan fitted with a stirrer, and 60 kilos. of fuming sulphuric acid are slowly run in, the temperature being kept at 110°. When the sulphonation is finished, the mass is diluted with water, neutralised with sodium carbonate, the solution boiled, and filtered. Salt is added to the hot filtrate, and, on cooling, the sodium salt of the monosulphonic acid separates out and is filtered off, pressed, and dried (Geigy & Co., F.P., 211913 ; G.P., 65017, 88085).

The acid is used for making Eriocyanine A.

4 : 4′-Tetramethyldiaminobenzhydrol,



This can be obtained by reducing tetramethyldiaminobenzophenone with zinc dust in alkaline amyl-alcoholic solution

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* Cohn (*Chem. Zeit.*, 1900, **24**, 564) employs 16 parts of dimethylaniline, 6 of formaldehyde (40 per cent.), and 20 of hydrochloric acid (25 per cent.).

(Badische Anilin- & Soda-Fabrik, E.P., 5450 of 1883; F.P., 158438; G.P. 27032), but is best prepared by oxidising tetramethyldiaminodiphenylmethane with lead peroxide.

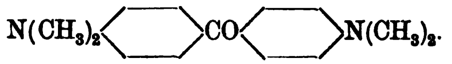
The following account is given by Möhlau and Heinze (*Ber.*, 1902, **35**, 359).

Twenty grams of tetramethyldiaminodiphenylmethane are dissolved in 50 grams of water and concentrated hydrochloric acid corresponding with 2 molecular proportions. The solution is diluted with 1,600 grams of water, and 9·4 grams (2 mols.) of glacial acetic acid are added. The solution is cooled to 0°, and a thin paste of lead peroxide, corresponding with 18·8 grams of the pure material, is vigorously stirred in. After five minutes, a solution of 26 grams of sodium sulphate ($Na_2SO_4,10H_2O$) in 120 grams of water is added. The lead sulphate is filtered off and the bluish-violet solution neutralised with cold, dilute sodium hydroxide, when the hydrol is precipitated in grey flocks. If it separates as a tar, this will harden after a few hours. It is filtered off and washed. The yield is 20 grams, or 94·3 per cent. of the theoretical.

4 : 4′-Tetramethyldiaminobenzhydrol melts at 96° and is readily soluble in alcohol or ether.

It is used for making Turquoise blue, Chrome green, Chrome violet, Chrome Bordeaux, Chrome blue, Crystal violet, Fast acid violet 10B, Agalma green B, Victoria blue R, Fast acid blue B, New patent blue B, New Fast blue, Naphthalene green V, and Wool green BS.

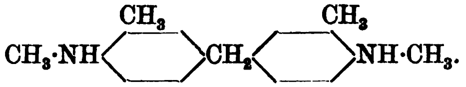
TETRAMETHYLDIAMINOBENZOPHENONE,
(MICHLER'S KETONE)



Carbonyl chloride is led into dimethylaniline at the ordinary temperature until the latter has increased in weight by 41 per cent. The autoclave is now closed and heated in a water-bath for five hours. On cooling, the excess of dimethylaniline is driven over with steam, the residue dissolved in hydrochloric acid, the solution filtered, and the ketone precipitated with sodium hydroxide solution (Michler, *Ber.*, 1876, **9**, 716, 1900). It is also obtained by warming a mixture of 10 kilos. of dimethylaminobenzanilide, 18 kilos. of dimethylaniline, and 8·5 kilos. of phosphoryl chloride for two hours in the water-bath. A good fusion is viscid, yellowish-brown, and of slight metallic lustre. The product is rendered alkaline and the dimethylaniline driven off with steam. The sandy residue is washed with water and added at 50–70° to a mixture of 50 litres of water and 5 kilos. of hydrochloric acid. An intensely yellowish-red solution is produced which quickly loses its colour, and now, by dilution with water and careful neutralisation with sodium hydroxide, a crystalline precipitate of the ketone is obtained which is filtered off. Aniline is recovered from the filtrate (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 1694 of 1887; F.P., 181351; G.P., 44077).

Michler's ketone melts at 175° and is readily soluble in alcohol or ether. It is used either alone or in the form of its chloride, $CCl_2[C_6H_4{\cdot}N(CH_3)_2]_2$ (prepared by the action of phosphorus trichloride, phosphoryl chloride, carbonyl chloride, etc.), for making Acid violets, Rheonine, Crystal violet, Victoria blue B and 4R, and Wool green S.

DIMETHYLDIAMINODI-*o*-TOLYLMETHANE,

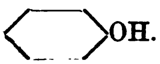


Formaldehyde (1 mol.; 40 per cent. solution) is mixed with methyl-*o*-toluidine (2 mols.), or a mixture of mono- and dimethyl-*o*-toluidine corresponding with this amount, and hydrogen chloride (1 mol.) is led into the cooled mixture. Alternatively, a mixture of methyl-*o*-toluidine (1 mol.), methyl-*o*-toluidine hydrochloride (1 mol.), and formaldehyde (1 mol.) is treated with the gas in the same way. The product is diluted with water, rendered alkaline with sodium carbonate, and the methyl-*o*-toluidine remaining is distilled in a current of steam. On cooling and after some time, the base remaining sets to a crystalline mass, which can be purified by crystallisation from alcohol or light petroleum (Badische Anilin- & Soda-Fabrik., E.P., 10465 of 1892; F.P., 222275; G.P., 67478; U.S.P., 488430). Braun (*Ber.*, 1908, **41**, 2153) states that this process gives a pure substance and practically no by-products.

It forms colourless tablets melting at 87°, boiling at 255°/9 mm., and is used for making Auramine G.

PHENOLS AND THEIR DERIVATIVES.

PHENOL,



Preparation of Benzenesulphonic Acid.—The sulphonation of benzene is performed in a closed, cast iron, steam-jacketed pan fitted with a helical stirrer with a speed of 180 revolutions per minute (Grandmougin, *Rev. prod. chim.*, 1916, **19**, 373).* The lid is fitted with a thermometer pipe, a reflux condenser, and a charging hole. The pan is fitted with a tap at the bottom for running out the finished batch. It is charged with 225 kilos. of sulphuric acid (100 per cent.), made, for example, by mixing 125 kilos. of 95 per cent. acid and 100 kilos. of fuming acid containing 30 per cent. of sulphur trioxide, and 100 kilos. of benzene. The stirrer must be kept running constantly. The temperature rises to 60–70°, and is then raised further by turning steam into the jacket, so as to keep the benzene gently boiling. The benzene condenses in the reflux condenser and runs back into the pan. At the end of seven to eight hours the benzene should have disappeared and the product should be completely soluble in water.

Alternatively, the pan may be charged with 260 kilos. of 98 per cent. acid and 40 kilos. of benzene. The remaining 60 kilos. are added gradually as the temperature ceases to rise, and finally the temperature is raised to 80° as above. Wendt (G.P., 71556) mixes benzene with 6 parts of sulphuric acid, adds infusorial earth until the mass is pasty but can still be stirred, and leaves it at the ordinary temperature for twenty-four hours, when a quantitative yield of the acid is obtained. A similar effect is produced by using animal charcoal (Aktiengesellschaft für Anilinfabrikation, G.P., 74639). Lamberts (G.P., 113784) heats 100 parts of benzene with 250 parts of sodium hydrogen disulphate, $NaH_3(SO_4)_2$ (prepared by heating sodium bisulphate with sulphuric acid, 60° Bé.), in a similar manner. (On subsequently neutralising the aqueous solution of the product with milk of lime, a solution of the sodium salt of benzenesulphonic acid constitutes the filtrate from the gypsum.) This method of sulphonation is not, however, generally used. Heinemann (E.P., 12260 of 1915) recommends the addition of a little iodine, whereby it is claimed that the sulphonation can be carried out with weaker acid and in a shorter time. Sulphuric acid (146 grams), benzene (70 grams), and iodine (0·25 gram) are heated under a reflux condenser for five hours, when the sulphonation is complete. The iodine can be recovered by adding water to the product and filtering. Another method consists in passing benzene vapour through sulphuric acid of any concentration at 120°; for example,

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* This process for the manufacture of phenol is identical with that described by Ney (*Met. and Chem. Eng.*, 1915, **13**, 686). An excellent description of the mechanical engineering of a synthetic phenol plant has been published by Pope (*ibid.*, 1916, **15**, 185).

the vapour of benzene is passed for twenty-seven hours through 100 parts of sulphuric acid of 62° Bé. (D 1·753) at 120°, and the excess of benzene is removed by a current of hot air; 130 parts of crystalline benzenesulphonic acid are obtained on cooling. The benzene vapour and steam passing away in the reaction are condensed and flow into a separator, where the water is removed. The upper layer of benzene passes through a drying chamber containing quicklime or calcium chloride, and thence returns to the boiler, where the benzene is vaporised (Compagnie des Produits Chimiques d'Alais et de la Camargue, E.P., 101973 [1916]). The same principle is employed by Tyrer (E.P., 103204 [1916], U.S.P., 1210725), who passes benzene vapour through concentrated sulphuric acid which is heated gradually from 100° to 185°. Finally, Aylsworth and Savings Investment and Trust Co. (U.S.P., 1260852) propose to add to a finished sulphonation in which excess of benzene has been used sufficient fuming sulphuric acid to convert the water of reaction into sulphuric acid, and then to proceed again with the sulphonation.

Conversion of the Sulphonation Mixture into Sodium Benzenesulphonate.—Several methods have been proposed for carrying out this conversion. Other things being equal, undoubtedly the best method is to neutralise with milk of lime, to filter off and wash the precipitated calcium sulphate, to convert the calcium salt into the sodium salt by adding sodium carbonate, and, after decanting or filtering from the calcium carbonate, to evaporate to dryness. However, in certain works special conditions may indicate the adoption of one or other of the alternative methods. Referring now to the sulphonation mixture obtained as described above (from 100 kilos. of benzene), the mass is run into about 300 litres of water contained in a lead-lined tub fitted with an agitator and perforated lead steam-coil, and nearly neutralised with milk of lime. The latter is prepared in an iron tank, 1 part of lime being slaked with 5 parts of water, about 140 kilos. of lime being required. Complete neutralisation is effected by adding precipitated calcium carbonate obtained from the next operation. The whole is heated to boiling, about 450 litres of cold water are added so as to render the calcium sulphate easily filterable, and filtered through a filter press at about 60°. The calcium sulphate is well washed and the wash-waters are used to dilute the next sulphonation or to slake the lime.

The filtrate contains the calcium benzenesulphonate. This is collected in a tub, stirred, and sodium carbonate added until a filtered sample gives no further precipitate with the alkali;

it should also give no precipitate with a solution of a calcium salt, showing that the liquid has been exactly neutralised. About 70 kilos. of sodium carbonate are required. The precipitated calcium carbonate is now allowed to settle, the clear liquid separated by decantation or filtration, evaporated, preferably in a multiple effect evaporator, and finally dried. Drum driers are used in America for this purpose. About 230–235 kilos. of sodium benzenesulphonate are obtained from 100 kilos. of benzene.

Instead of sodium carbonate, the sulphate may be used in the above operation, and, further, the correct amounts of lime and sodium sulphate may be added to the diluted sulphonation mixture (Sachs and Byron, U.S.P., 1207798).

Tyrer (E.P., 101807 [1916]) proposes to add to 100 parts of the sulphonation mixture (containing 85 per cent. of benzenesulphonic acid and 12 per cent. of sulphuric acid) 50 parts of finely powdered quicklime gradually, and then 500 parts of a solution of nitre-cake containing 64 parts of sodium hydrogen sulphate. The mass is filtered, the gypsum washed, and the filtrate evaporated to dryness.

Alternatively, twice the above amount of bisulphate may be added first and then the quicklime, and the whole submitted to the action of steam at 100 lb. pressure for half an hour. The filtrate contains sodium hydroxide in addition to sodium benzenesulphonate and sodium sulphate, the former being about 12 per cent. of the total requirement for the subsequent melting operation. The remaining amount is added, the solution concentrated, filtered from most of the sodium sulphate which is precipitated, and evaporated to dryness. The dry mixture is then fused. The whole of the sodium hydroxide necessary can be made from the nitre cake (244 parts in this case) by adding 100 parts of quicklime, and, after filtering, 145 parts of barium hydroxide, and again filtering.

The alternative main method of working up the sulphonation mixture is to precipitate it directly with a sodium salt. Thus the sulphonation mixture from 100 kilos. of benzene is poured into a lead-lined tank (25 cm. deep), fitted with an agitator and containing about 250 litres of water and 150 kilos. of anhydrous sodium sulphate. On cooling, the sodium benzenesulphonate is centrifuged or filtered. The product contains about 84 per cent. of the sodium salt, and the yield is about 210–220 kilos. (calculated as dry), which can be increased with good working. The separation is rather slow, and it is necessary to have a large surface for this purpose. About 180 square metres are required for 1 ton of benzene. The filtrate from this operation is used by Ellis (U.S.P., 1179415) to acidify the sodium phenoxide from the fusion.

Sodium carbonate (100 kilos.) may be used instead of the sulphate partly to neutralise the mass; for example, Uhlmann (E.P., 24826 of 1906; F.P., 371089; G.P., 229537) (who uses also sodium sulphite) pours the sulphonation mixture from 800 kilos. of benzene and 2,000 kilos. of sulphuric acid (66° Bé.) into a solution or suspension of about 1,700 kilos. of sodium carbonate in 5,000 litres of water. The gases are led away, the mixture is boiled, and filtered from the anhydrous sodium sulphate which separates out. This is washed with a boiling solution of sodium sulphate, and this wash-water is used in the next operation for dissolving the sodium carbonate.

In these " salting-out " methods about 5 per cent. of material is lost in the mother liquors, and another disadvantage lies in the fact that, unless the mass is completely neutralised with sodium carbonate, the product cannot be freed from sulphuric acid.

Ellis (U.S.P., 1191880) liberates the phenol from the sodium phenoxide by means of carbon dioxide, and uses the sodium carbonate so formed to neutralise the sulphonation mixture. Miersch (E.P., 2565 of 1907; F.P., 373338; G.P., 199959; U.S.P., 889799) heats 58 kilos. of the sulphonation mixture, to which about 10 per cent. of water is added, with about 12 kilos. of sodium chloride which has been added gradually. Hydrochloric acid is evolved, and at 130–140°, sometimes only at a slightly higher temperature, two layers are formed. The evolution of hydrochloric acid is then nearly complete, and the upper layer of benzenesulphonic acid and its sodium salt, together with a little sulphuric acid, can be separated from the lower layer of sodium hydrogen sulphate while both are hot and liquid.

An altogether different method for removing the benzenesulphonic acid from the sulphonation mixture is that proposed by Dennis (E.P., 109709 [1916]; U.S.P., 1212612). The mixture of acids is treated with a solvent such as benzene, which dissolves the benzenesulphonic acid, and this solution is treated with a suitable substance to form a salt not soluble in the solvent. In a later patent, the same author (U.S.P., 1229593) treats the benzene solution with water and then extracts the sulphonic acid from this. A very similar process has been patented by Bull (E.P., 118727 [1917]; U.S.P., 1247499).*

Fusion with Sodium Hydroxide.—This is done in an open† cast iron pan fitted with an agitator and heated by gas. Local overheating must be avoided, as this gives rise to the formation of thiophenol. Two hundred and twenty kilos. of sodium hydroxide (90 per cent.) are placed in the pan, 20 litres of water added, and the mixture is heated to 290°. Into the molten alkali 280 kilos. of sodium benzenesulphonate are introduced, care being taken that the temperature does not drop, but rises gradually to 300°. When the addition is finished the temperature may be raised to 315–330°, but must not go beyond 340°. The reaction proceeds fairly rapidly and the mass becomes fluid and homogeneous at the end. The fusion takes three to four hours as a rule. It is now run, while still fluid, into cold water, 3 parts of the latter being used for 1 part of sodium hydroxide employed in the fusion. The temperature of the water rises to nearly 100°, and the solution has a density of 27° Bé.

The sodium phenoxide is thus dissolved, whilst most of the sodium sulphite separates in the anhydrous condition. The whole is filtered and the sulphite is mixed with water at 85° and filtered again (this remains in the anhydrous state above 40°). The wash-waters are added to the solution of sodium phenoxide. This solution is treated with sulphuric acid (about 190 kilos. of 50° Bé.) until it is neutral to litmus, and after a few hours the phenol, which forms as a yellowish, oily layer on the top of the aqueous solution, is separated. By allowing the aqueous solution to crystallise, sodium sulphate is obtained which can be again used in the process.

Dennis (U.S.P., 1227894) acidifies with an aqueous solution of benzenesulphonic acid, thus producing phenol and sodium benzenesulphonate, and it has already been mentioned that carbon dioxide is used, whilst Howard (U.S.P., 1245343) employs an alkali bicarbonate.

Tyrer (E.P., 104220 [1916]; F.P., 487566; U.S.P., 1210726) uses a mixture of carbon dioxide and sulphur dioxide prepared by treating a mixture of calcium carbonate and calcium sulphite with sodium hydrogen sulphite. A mixture of sodium sulphite

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* A description of the Dennis-Bull process is given by Peterkin (*Chem. and Met. Eng.*, 1918, **19**, 255).

† Recent laboratory experiments show that the yield is increased by effecting the fusion in an atmosphere free from oxygen (Boswell and Dickson, *J. Amer. Chem. Soc.*, 1918, **40**, 1786).

and sodium carbonate is thus formed in solution, which is treated with lime to give sodium hydroxide, and a mixture of calcium carbonate and calcium sulphite.

The Merrimac Chemical Co. (U.S.P., 1245353) employs sulphur dioxide obtained by neutralising the sulphonation mixture with calcium sulphite. The sodium sulphite produced is used to convert the calcium benzenesulphonate into the sodium salt and calcium sulphite.

The phenol, having been separated, is washed with water and distilled, preferably in a vacuum. A silver, or silvered, coil may be used. The first and last runnings are collected separately and put back into the next charge. The yield by the "salting-out" method is 82–83 per cent., that is, the same weight of phenol is obtained as of benzene taken. A little higher yield (103 parts of phenol from 100 of benzene) can be obtained with practice. The maximum yield of sodium benzenesulphonate is 98 per cent., and the yield in the fusion 87 per cent., so that the yield of phenol is 85 per cent. This figure is easily obtained by using the liming-out process.

Another process that has been suggested for obtaining phenol is to heat chlorobenzene with sodium hydroxide in an autoclave.

It is claimed by Meyer and Bergius (E.P., 25555 of 1912; F.P., 450305; U.S.P., 1062351; *Chem. Zeit.*, 1914, **38**, 1040; *Ber.*, 1914, **47**, 3155) that the best results are obtained with 15–20 per cent. sodium hydroxide. With 4 molecular proportions of sodium hydroxide and twenty hours' heating at 300° a 96 per cent. yield of pure phenol is obtained. It is best to work in autoclaves without stirrers, as otherwise the alkali attacks the metal. The pressure has to be very high, namely, 200–300 atmospheres.

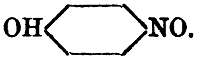
J. W. Aylsworth, A. M. Aylsworth, and the Savings Investments and Trusts Co. Exors. (E.P., 103664 [1917]; U.S.P., 1213142, 1213143) use, for 1 molecule of chlorobenzene, 2–3 mols. of sodium hydroxide and about 20 mols. of water and pump the mixture through heated coils at 300°. The Chemische Werke Ichendorf (G.P., 281175) adds methyl alcohol to the mixture.

Finally, Terrisse (E.P., 108938 [1916]) oxidises cresols in sodium hydroxide fusion with copper oxide or lead peroxide, to hydroxybenzoic acids, which are then heated in a stream of carbon dioxide at 300° and are converted into phenol.

Phenol melts at 42·5° and boils at 181°/760 mm. or 120·2°/100 mm. At the ordinary temperature, it has D 1·066 and dissolves in 15 parts of water. The solubility rises rapidly with the temperature, and at 84° phenol and water mix in all proportions.

Phenol is used for the manufacture of nitrophenols, picric acid, salicylic acid, Corallin, Diazine black, Brilliant yellow, Chrysophenine G, Diamine scarlet B, Congo orange R, Diamine yellow N, Diamine gold yellow, Erie direct green ET, Chloramine green B, Diamine green B (Oxamine green B), Diphenylchrysoin 2R, and Methyl violet.

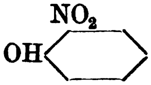
p-NITROSOPHENOL,



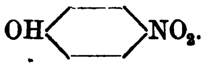
Ninety-four kilos. of phenol are dissolved in 1,000 litres of water and 85 kilos. of concentrated sodium hydroxide solution and a solution of 75 kilos. of sodium nitrite in 300 litres of water and 1,000 kilos. of ice are added; a mixture of 235 kilos. of concentrated sulphuric acid and 650 kilos. of ice is now run in within an hour and a half, the temperature not being allowed to exceed 5°. The precipitated *p*-nitrosophenol is filtered off, centrifuged and dried in the air (Lange, " Die Schwefelfarbstoffe," 1911, p. 133). A very similar laboratory recipe is given by Bridge (*Annalen*, 1893, **277**, 85).

p-Nitrosophenol melts at 126° and is used for making Hydron blue.

o- *and* *p*-NITROPHENOL,



and



Phenol is nitrated by means of 2 parts of nitric acid (D 1·38) and 4 parts of water. The phenol is first liquefied with a little water and run gradually into the mixture of the nitric acid with 3 parts of water which is at about 8°. The fourth part of water is used in the form of broken ice, which is added as required to keep the temperature below 35°. When all the phenol has been added, the mixture is allowed to settle for one to two hours, the liquid on the surface of the oil is siphoned off and the oil is washed several times with water. Water is added and the *o*-nitrophenol distilled over by means of indirect steam. The crude material must be distilled again with steam, as it contains some phenol. The yield is 36–44 per cent. of the phenol employed.

The *p*-nitrophenol remains behind and is extracted several times with hot water, the solution filtered, and the *p*-nitrophenol crystallises out. The mother liquors, on evaporation, furnish a further quantity. Paul (*Zeitsch. angew. Chem.*, 1896, **9**, 588) states that the *p*-nitrophenol can be freed from the tarry matter by repeated crystallisation from a little naphtha, and also by dissolving 800 grams of the crude substance in 8–10 litres of water and 250 grams of chalk by means of a current of steam, filtering, and adding to the filtrate 200 grams of sodium carbonate and 5 kilos. of salt. On filtering, the pure sodium salt of *p*-nitrophenol crystallises out.

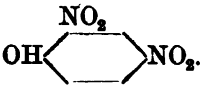
p-Nitrophenol, unaccompanied by the ortho-compound, can be obtained by hydrolysing *p*-nitroacetanilide with two molecular proportions of sodium hydroxide and also as follows: One hundred kilos. of phenol and 42 kilos. of sodium hydroxide are dissolved in 1,000 litres of water, the solution is heated by means of a steam-jet, and 210 kilos. of toluene-*p*-sulphonyl chloride (a by-product in the manufacture of saccharin) are added gradually, and the heating is continued until no odour of the sulphonyl chloride remains. On cooling, the ester is filtered off, washed with water, and dried. A mixture of 100 kilos. of this ester and 100 kilos. of potassium nitrate (or the corresponding quantity of nitric acid) is added gradually to 1,000 kilos. of sulphuric acid, the temperature being kept at 15°. When the nitration is finished the product is separated from sulphuric acid by filtration or centrifuging and well washed with water.. This is the *p*-nitrophenyl ester of *o*-nitrotoluene-*p*-sulphonic acid, which, when dried and crystallised from benzene, melts at 115°. The moist product is suspended in an equal weight of sodium hydroxide solution (36° Bé.), or 100 kilos. of the ester are mixed with a solution of 30 kilos. of sodium hydroxide and heated to 100° until all is dissolved. On cooling, sodium *p*-nitrophenoxide crystallises out and is filtered off from the sodium *o*-nitrotoluene-*p*-sulphonate which remains in solution. The free acids are obtained by treatment with a mineral acid (Société Chimique des Usines du Rhône, E.P., 24193 of 1895; G.P., 91314). *o*-Nitrophenol is also obtained by nitrating phenol-*p*-sulphonic acid and subsequent hydrolysis with superheated steam (Farbenfabriken vorm. F. Bayer & Co., G.P., 43515), but Paul (*Zeitsch. angew. Chem.*, 1896, **9**, 588) was able to obtain only a 25–33 per cent. yield of the theoretical by this process.

The pure compounds are obtained by boiling *o*- and *p*-chloronitrobenzene respectively with sodium hydroxide solution (compare the preparation of 2 : 4-dinitrophenol, p. 113).

o-Nitrophenol melts at 44·27°, boils at 214°, and has D 1·657. It dissolves in 92 parts of water at 100°. It is used for making *o*-nitroanisole and *o*-aminophenol; also Thional black.

p-Nitrophenol melts at 114° and has D 1·468. It is used for making *p*-aminophenol and Italian green.

2 : 4-DINITROPHENOL,



Although dinitrophenol is now manufactured from 4-chloro-1 : 3-dinitrobenzene, its preparation also from phenol may be described (Reverdin and de la Harpe, *Chem. Zeit.*, 1892, **16**, 45). Two hundred parts of phenol are added to 400 parts of sulphuric acid (95 per cent.) which has been heated to 110° and after five hours the temperature is raised to 130–140°. The mixture is now diluted with 600 parts of water, and a mixture of 800 parts of nitric acid (53 per cent.) and 575 parts of water (that is, 1,375 parts of nitric acid of D 1·197) added so that the temperature does not rise above 45–50°. The whole is left for twenty-four hours at the ordinary temperature, after which it is warmed slowly by means of a water-jacket for three days, allowed to cool, and filtered. The product, which forms a crystalline cake, is almost pure dinitrophenol. It is purified by boiling it twice with 2,000 parts of water. The yield is 100 parts of dinitrophenol. The filtrate, which contains picric acid, may be evaporated to convert any remaining dinitrophenol into picric acid.

According to Vidal (F.P., 315696), a solution of 93 kilos. of phenol in 192 kilos. of sulphuric acid (95 per cent.) is run into a solution of 172 kilos. of sodium nitrate in 1,700 litres of water. The mixture is allowed to remain for several hours and then slowly heated until the gas evolution ceases. On cooling, the dinitrophenol is filtered off.

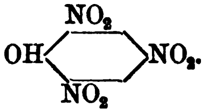
Another process for obtaining dinitrophenol direct from benzene is described by Wolffenstein and Böters (*Ber.*, 1913, **46**, 586). One hundred and twenty grams of benzene are mixed with 20 grams of mercuric nitrate, and the mixture is treated with 270 grams of nitrogen tetroxide and allowed to remain for some days at the ordinary temperature, or the same weight of benzene is treated with 10 grams of mercuric nitrate and 500 grams of 50 per cent. nitric acid; 50 grams of nitric oxide are added, and the mixture is stirred and heated to 50°.

The usual method for manufacturing dinitrophenol is, however, as stated above, namely, to substitute the hydroxyl group for the chlorine atom in chlorodinitrobenzene. For this purpose, 100 parts of chlorodinitrobenzene are mixed with a solution of 125 parts of sodium carbonate (anhydrous) in 1,000 parts of water, and the whole is boiled under a reflux condenser for twenty-four hours until the chloro-derivative has been completely decomposed. The operation may be conducted in a lead-lined iron pan fitted with a reflux condenser made of lead pipe. The product is blown into a tub, acidified, and the precipitated dinitrophenol collected in a filter press. The yield is practically quantitative.

Another method is to boil 48 parts of chlorodinitrobenzene with 150 parts of water and 62 parts of sodium hydroxide (Claus, E.P., 11590 of 1909), and milk of lime may also be employed.

2 : 4-Dinitrophenol melts at 114° and dissolves in 197 parts of water at 18° and in 21 parts of boiling water. It is used mostly for making Sulphur blacks. On reduction with ammonium sulphide, it gives *p*-nitro-*o*-aminophenol, m. p. 142–143° (Post and Stuckenberg, *Annalen*, 1880, **205**, 66 ; compare also Auwers and Röhrig, *Ber.*, 1897, **30**, 995), which is used for making Palatine chrome green G (Chrome fast green G).

PICRIC ACID,



The following description of the manufacture of picric acid is given by Escales (" Nitrosprengstoffe," 1915, p. 177).

Twelve parts by weight of phenol are heated with 48 parts of sulphuric acid (D 1·84) for eight hours at 100–105° in a lead-lined cast iron pan fitted with a stirrer and steam-jacket. The mixture is run into a movable earthenware vessel, as it partly solidifies on cooling. It is transferred from this by means of ladles into 90 parts of nitric acid (D 1·385) contained in an earthenware vessel set in a water-bath and the whole well stirred to obtain a homogeneous mixture. During this operation, in which the phenoldisulphonic acid is converted into dinitrophenolsulphonic acid, the temperature should not rise above 20°, and this is obtained by carefully cooling the vessel. When all the sulphonic acid has been added (100 kilos. take about twenty hours), steam is slowly led into the water surrounding the vessel so that the temperature of the contents rises to 40–50° within four hours, and then the water is heated to boiling. Large quantities of nitrous fumes are evolved at 80–90°, which should be led off through earthenware pipes to absorption towers. When the vigorous reaction has subsided and the lid of the nitrating vessel begins to cool, the water is kept boiling for three to four hours longer and the nitration mixture stirred from time to time with a strong glass or porcelain rod. Heating is then stopped and the mixture allowed to cool to 30–35°, when the picric acid crystallises out almost completely.

The waste acid is siphoned off, and the crystals are brought on a filter and washed with a little water several times in order to remove the bulk of the sulphuric acid. The crystals are then transferred to a centrifuge fitted with a woollen cloth, and there washed with a little cold water until the filtrate contains only traces of sulphuric acid. It may be noted that picric acid is much more readily soluble in pure water than in water containing sulphuric acid. The crystals, which still contain 10–15 per cent. of water, are then dried at a low temperature on glass plates. The yield from 100 parts of phenol is 190 parts of picric acid, melting at 121–122°.

If the waste acid is allowed to settle for some days a small amount of picric acid is deposited and may be recrystallised from water.

Great care must be taken not to allow metals, particularly lead, to come into contact with picric acid, as the salts are extremely explosive.

Ney (*Met. and Chem. Eng.*, 1915, **13**, 686) gives the following account of the process.

One part of phenol is sulphonated with 4 parts of sulphuric acid (98 per cent.) in a large steam-jacketed vessel provided with an agitator. The resulting sulphonic acid is treated in a nitrating vessel provided with heating and cooling coils, with an equal amount of sulphuric acid, cooled to 20°, and the nitrating acid, usually a mixture of equal parts of nitric and sulphuric acids, is run in. Instead of the three molecules of nitric acid required by theory, four are used. The contents of the vessel are kept below 40° while the first 30–40 per cent. of the nitric acid is added, and then raised gradually to 70–80°. The contents are then transferred to a non-metallic, acid-proof vessel and diluted with an equal volume of water. The crystals which separate on cooling are drained on a vacuum filter. A purer product is obtained by melting the crystals and running the melted material through a sieve of gold or platinum into cold water in a wooden tank. Large makers of picric acid use a filtering box in which a vacuum can be applied both above and below. The crystals are first drained by the vacuum and then washed with alcohol spray.

which removes the resin formed in the nitrating process.* A cover is then put on and vacuum applied above so as rapidly to dry the crystals.

Good results have been obtained by nitrating phenol without using sulphuric acid according to Gutensohn's process (E.P., 16628 of 1900; G.P., 126197). Phenol is dissolved in paraffin, the solution added to the requisite amount of nitric acid, and the whole covered with a layer of paraffin. Much heat is evolved, so that external heating is not necessary; but it is advantageous for the reaction vessel at the beginning of the operation to be set in a water-bath at 27°. It is also advisable to add a little sulphuric acid to the nitric acid, in the proportion of 1½ parts of the former to 12 parts of the latter.

An increased yield of picric acid is said to be obtained by heating phenol with pyrosulphuric acid at 100–110° and nitrating the resulting phenoltrisulphonic acid at 100° by the gradual addition of the calculated quantity of sodium nitrate (Eisenmann and Arche, E.P., 4539 of 1889; F.P., 198147; G.P., 51321).

Köhler (G.P., 67074) describes a process of heating 100 parts of phenol with 1,000 parts of concentrated sulphuric acid for two hours at 170°, which gives rise to phenoldisulphonic acid; 96 parts (1 molecule) of dry, powdered sodium nitrate are now added and the mixture is heated to 140°. This nitrophenoldisulphonic acid is diluted with 320 parts of water and heated to 80–90° with 244 parts of sodium nitrate, the temperature being allowed to reach 140° in about two hours.

It was shown by Henking (*Zeitsch. Chem.*, 1872, [ii], 8, 523) that 2 : 4-dinitrophenol, on further nitration, gives picric acid, and this reaction is also utilised for the preparation.

Another method consists in converting aniline into sulphanilic acid and treating the diazo-compound with nitric acid, whereby picric acid is readily obtained; 50 parts of aniline yield 110 parts of picric acid (Wenghöffer, E.P., 16371 of 1900; F.P., 303683; G.P., 125096; U.S.P., 666627).

In the process of Wolffenstein and Böters (E.P., 17521 of 1907; F.P., 380121; G.P., 194883; U.S.P., 923761), 400 grams of benzene, 1,350 grams of nitric acid (D 1·39), and 50 grams of mercuric nitrate are mixed and warmed on the water-bath. The products are 380 grams of picric acid, 160 grams of nitrobenzene, and 2 grams of *o*-nitrophenol. The nitrobenzene

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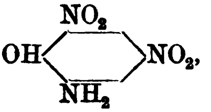
* The nitration in the above process is carried out with no water and much more sulphuric acid than is usual, which probably accounts for any resin that may be formed.

is removed by distillation with steam, leaving crude picric acid as the residue.

Picric acid melts at 122·5° and has D 1·813. The amount of water necessary to dissolve it at various temperatures is shown in the following table (Doliński, *Ber.*, 1905, **38**, 1836).

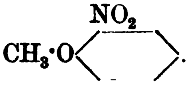
Temperature.........	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
Parts of water	147·0	123·4	90·0	71·4	56·2	46·5	35·0	28·8	22·6	17·4	13·8

It is used largely as an explosive and, in limited quantities, for making picramic acid.

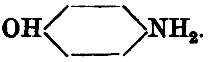
On reduction with zinc powder and ammonia (Frébault and Aloy, *J. Pharm. Chim.*, 1904, [vi], **20**, 245 ; *Bull. Soc. chim.*, 1905, [iii], **33**, 495), alcoholic ammonium sulphide (Egerer, *J. Biol. Chem.*, 1918, **35**, 565), or aqueous sodium hydrogen sulphide in the cold it yields picramic acid,  $\mathrm{OH}\overset{NO_2}{\underset{NH_2}{\langle\quad\rangle}}\mathrm{NO_2}$, but no exact details of the manufacture have been published.

Picramic acid is readily soluble in hot water and crystallises in red needles melting at 168–169°.

It is used for making Acid anthracene brown R, Metachrome brown B, Metachrome Bordeaux, Chrome brown P, and Anthracyl chrome green.

o-NITROANISOLE,  $CH_3{\cdot}O\overset{NO_2}{\langle\quad\rangle}$.

See under Dianisidine, p. 96.

p-AMINOPHENOL, 

(1) *From* p-*Nitrophenol*.—The manufacture of *p*-aminophenol by reducing *p*-nitrophenol with tin and hydrochloric acid is described by Paul (*Zeitsch. angew. Chem.*, 1896, **9**, 594). One hundred and eighty kilos. of hydrochloric acid (20° Bé.) and 75 kilos. of moist tin are placed in an earthenware vessel of 300 litres capacity, and 25 kilos. of *p*-nitrophenol are gradually stirred in. The temperature rises to 100–106° and when all is in 200 kilos. of sulphuric acid (66° Bé.) are added in a thin stream, the whole being well stirred. After three days, the *p*-aminophenol sulphate will have crystallised out. It is filtered on a

wool filter, centrifuged, dissolved in 200 litres of cold water, and the base liberated with sodium carbonate; some tin is also precipitated. One kilo. of sodium hydrogen sulphite, dissolved in water, is added to protect the base from oxidation. The base is filtered off and the cake dissolved in 200–300 litres of boiling water with the addition of 10 kilos. of sodium hydrogen sulphite. On filtering and cooling, *p*-aminophenol crystallises in white needles. The mother liquor is used to dissolve the crude sulphate in the next batch.

To prepare the pure sulphate, the crystallised base is boiled with 4–5 parts of water with the addition of 1 kilo. of sodium hydrogen sulphite, and sulphuric acid, somewhat diluted, is added until an acid reaction to Congo paper is obtained. On cooling the filtered solution, the sulphate separates in colourless crystals which are filtered, centrifuged, and dried. The yield is 12·5 kilos. The base remaining in the liquor is precipitated by sodium carbonate and put into the next batch. The tin is precipitated from the waste liquor containing it by means of scrap zinc, and is filtered off and used again.

The reduction of *p*-nitrophenol can also be effected by sodium hyposulphite (hydrosulphite) in alkaline solution (Grandmougin, *J. pr. Chem.*, 1907, [ii], **76**, 135), by iron and acetic acid, or by means of iron, ferrous chloride, and hydrochloric acid (compare the preparation of aniline, p. 39), and Brochet (E.P., 16936 of 1913; F.P., 458033; U.S.P., 1247629) mentions that *p*-aminophenol can be obtained by the catalytic reduction of *p*-nitrophenol by means of nickel.

(2) *From* p-*Nitrosophenol*.—This is dissolved in 30 parts of water containing a little sodium sulphide, and a concentrated solution of 4 parts of crystallised sodium sulphide is slowly added until the yellow colour of the nitrosophenol has disappeared. After cooling, the solution is just acidified with hydrochloric acid, the precipitate filtered off, extracted with boiling water and the solution filtered, when *p*-aminophenol separates on cooling.

(3) *From* p-*Azophenol*.—Täuber (G.P., 82426) obtains *p*-aminophenol by reducing *p*-azophenol, $OH{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}OH$ (prepared by combining diazotised sulphanilic acid with phenol and fusing the product with sodium hydroxide), with stannous chloride or with zinc dust and sodium hydroxide.

(4) *From* p-*Hydroxyazobenzene*.—This is dissolved in a slight excess of dilute sodium hydroxide, and sodium hyposulphite (hydrosulphite) is added to the boiling solution until it is decolor-

ised. The aniline is driven over with steam, the liquid filtered, and, on cooling, *p*-aminophenol crystallises out (Grandmougin, *J. pr. Chem.*, 1907, [ii], **76**, 126). Vidal reduced this azo-compound by heating with sodium sulphide and sodium hydroxide to 180° (E.P., 5697 of 1897; F.P., 264511; G.P., 95755; U.S.P., 595897).

(5) *From Nitrobenzene.*—This method consists in dissolving 30 kilos. of nitrobenzene in 250 kilos. of sulphuric acid, adding 50 kilos. of zinc dust at 50–80° within four hours, and keeping the mixture for ten hours at this temperature. It is then cooled and poured on ice, when the *p*-aminophenol sulphate separates out (Farbwerke vorm. Meister, Lucius, & Brüning, G.P., 96853).

(6) *From* p-*Chlorophenol.*—A mixture of *p*-chlorophenol (50 parts), 25 per cent. solution of ammonia (370 parts), and copper sulphate (8 parts) is heated in an autoclave for twelve hours at 140°. After acidification and removal of unaltered *p*-chlorophenol by a current of steam, *p*-aminophenol is obtained by neutralising with sodium carbonate; a little sodium sulphite is also added (Aktiengesellschaft für Anilinfabrikation, E.P. 4044 of 1908; F.P., 397524; G.P., 205415).

(7) *From Nitrobenzene by Electrolytic Reduction.*—The electrolytic reduction of nitrobenzene on the small scale is described by Gattermann (*Ber.*, 1893, **26**, 1847) and by Stroji (*J. Chem. Ind. Tokyo*, 1918, **21**, 117; *J. Soc. Chem. Ind.*, 1918, **37**, 459A).

According to Darmstädter (G.P., 150800), the production of aniline can be avoided by using carbon cathodes. A suspension of 100 grams of nitrobenzene in 1 kilo. of 85 per cent. sulphuric acid requires a current density of 4 amperes per sq. dcm. In a later patent Darmstädter (G.P., 154086) uses 1,000 c.c. of 50 per cent. sulphuric acid and 250 grams of nitrobenzene in the cathode space; and 40 per cent. sulphuric acid in the anode space, which is diluted as it becomes concentrated in the electrolysis. The cathodes are carbon and the anodes lead plates. With a current of 6 amperes per sq. dcm., about 200 ampere-hours are required to reduce about 200 grams of nitrobenzene. After cooling, the nitrobenzene is separated and the *p*-aminophenol sulphate is filtered off. The solution is strengthened by the addition of sulphuric acid and used again.

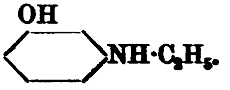
The Society of Chemical Industry in Basle gives the following process (E.P., 18081 of 1915; G.P., 295841).

The electrolytic vessel is a lead cylinder which serves as the anode. In it is placed a porous cylinder containing a copper cathode in the form of a hollow perforated cylinder, and within this is a suitable stirrer. One or more rods of lead dip into the cathode chamber. The anode chamber is charged with 30 per cent. sulphuric acid and the cathode chamber with 25 litres of sulphuric acid (15° Bé.) and 6 kilos. of nitrobenzene, which is kept in the form of an emulsion by means of the stirrer. The electrolysis is carried on at 80–95° with a current of about 3 amperes per sq. dcm. of cathode surface at 3–3½ volts until all the nitrobenzene has disappeared. Milk of lime is now added and the aniline distilled off in a current of steam. The remaining hot solution of *p*-aminophenol is filtered from calcium sulphate and evaporated to crystallisation. The yield of *p*-aminophenol is about 50 per cent. of the weight of nitrobenzene used (about 56 per cent. of the theoretical), and aniline is produced to the extent of about 20 per cent. of the weight of *p*-aminophenol formed. If arsenic is present (for example, in the sulphuric acid) the amount of aniline obtained will fall to about 10–15 per cent. of the weight of *p*-aminophenol. Instead of the arrangement described, the cathode may be of lead and a copper rod may be suspended in the cathode chamber, or copper sulphate may be added to the chamber and renewed from time to time.

p-Aminophenol melts at 184°. It rapidly oxidises in the air and can be obtained in white, crystalline plates by treating a concentrated solution of the hydrochloride with a saturated solution of sodium sulphite (Lumière and Seyewetz, *Compt. rend.*, 1893, 116, 1202).

It is used under the name Ursol P for dyeing fur, and under the name Rodinal as a photographic developer; also for making 2 : 4-dinitro-4′-hydroxydiphenylamine (by condensation with 4-chloro-1 : 3-dinitrobenzene), Pyrogen green, and Immedial indone.

MONOETHYL-*m*-AMINOPHENOL,



(1) Ten kilos. of monoethylaniline are added to 20 kilos. of fuming sulphuric acid (containing 23 per cent. of sulphur trioxide), the temperature not being allowed to rise above 60°. The mixture is cooled and 30 kilos. of fuming sulphuric acid (containing 75 per cent. of sulphur trioxide) are added, and the whole allowed to remain at 40° until a sample gives a clear solution in alkaline water. It is then poured into water and the sodium ethylaniline-*m*-sulphonate is isolated as sodium salt in the usual

way. Ten kilos. of the dry sodium salt are melted with 25 kilos. of potassium hydroxide for ten hours at 200–220°, preferably in the absence of air. The product is dissolved in water, the solution acidified with hydrochloric acid, and filtered. It is neutralised with sodium carbonate, and the monoethyl-*m*-aminophenol is extracted with ether or benzene. The solvent is distilled off and leaves the phenol as an oil which, after distillation, gradually solidifies (Badische Anilin- & Soda-Fabrik, G.P., 48151; compare also Gnehm and Scheutz, *J. pr. Chem.*, 1901, [ii], **63**, 423).

(2) Twenty kilos. of sodium *m*-phenyleneoxamate,

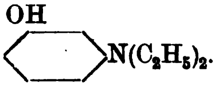
$$C_6H_4(NH{\cdot}CO{\cdot}CO_2Na)_2,$$

are mixed with 20 kilos. of sodium ethyl sulphate, 20 kilos. of alcohol, and 2–5 kilos. of sodium carbonate, and the whole is heated for six hours at 180° in an autoclave fitted with a stirrer, The alcohol is distilled off and the mass extracted with water, leaving a residue of the ethylated compound. This is boiled with an equal weight of sulphuric acid and 3–4 times the weight of water for some time and most of the water distilled off. The solution, containing ethyl-*m*-phenylenediamine sulphate, is cooled with ice, sodium nitrite (1 mol.) added, and the solution warmed until nitrogen ceases to be evolved. It is then neutralised with sodium carbonate and the base isolated as above (Badische Anilin- & Soda-Fabrik, G.P., 76419).

(3) 18·9 Kilos. of aniline-2 : 5-disulphonic acid are neutralised with 5·6 kilos. of potassium hydroxide in aqueous solution and the whole is diluted to 200 litres; 18·5 kilos. of sodium ethyl sulphate (80 per cent.) are stirred in and the mixture is heated in an autoclave for eight to ten hours at 170–180°. After cooling, sodium carbonate is added to precipitate the ethyl-*m*-aminophenol, which is isolated and purified (Farbenfabriken vorm. F. Bayer & Co., G.P., 82765).

Ethyl-*m*-aminophenol melts at 62° and boils at 176°/12 mm. It is used for making Rhodamine 6G.

DIETHYL-*m*-AMINOPHENOL,



This is formed (1) by heating *m*-aminophenol hydrochloride with ethyl alcohol in an autoclave (Badische Anilin- & Soda-Fabrik, E.P., 15374 of 1887; F.P., 186697; G.P., 44002). (2) by heating resorcinol with diethylamine (Leonhardt & Co., E.P., 8156 of 1889; F.P., 198178, 198290; G.P., 49060); or (3) by alkali fusion of diethylaniline-*m*-sulphonic acid, obtained by sulphonating diethylaniline with fuming sulphuric acid (Society of Chemical Industry in Basle, F.P., 190096; G.P., 44792; U.S.P., 403678).

The latter is the method which is employed on the large scale and Wolfrum ("Chemisches Praktikum," Part II, p. 326) gives the following detailed description of the manufacture of this compound.

Two hundred and forty kilos. of diethylaniline are run in a thin stream into 240 kilos. of sulphuric acid. The temperature does not rise above 75°. The sulphate so produced is transferred to a sulphonating pan and 700 kilos. of fuming sulphuric acid (containing 40 per cent. of sulphur trioxide) are added, the whole being well stirred during the operation. The temperature of the mixture at the end of the addition will have risen to 125°, and is kept at this point for four hours. When the mixture has cooled to 70°, half of it is blown into milk of lime prepared from 400 kilos. of slaked lime and 3,000–3,200 litres of water. When the lime is exactly neutralised, a solution of 60 kilos. of anhydrous sodium carbonate is added so as to obtain the sodium salt of diethylanilinesulphonic acid in solution. The mixture is filtered and the filtrate evaporated. The remaining half of the sulphonation is treated in the same way. To the concentrated solution of the sodium salt 175 kilos. of sodium hydroxide are added, and the solution is evaporated until the temperature rises to 160–170°. The mixture is thus sufficiently dried to prevent too much foaming taking place on subsequently melting. The mixture prepared in this way from four or five sulphonations is then heated slowly to 300° in an oven. For this purpose, the mixture is contained in lots of 25 kilos. in special cast iron melt-tubes placed in the oven. The finished melts are dissolved in a narrow, high vessel. The solution is acidified in five lots with sulphuric acid (280–300 kilos. for each) and the sulphur dioxide expelled by boiling. The solution is then pumped into a semicircular lead-lined vessel and sodium carbonate solution added until there is only a slight acid reaction. The oily aminophenol sulphate separates and rests on the surface of the concentrated sodium sulphate solution. The latter is drawn off and the oil remaining is treated with dry sodium carbonate until a test portion shows no separation of oil on dilution with water.

About 80 kilos. of sodium carbonate are required for each of the above five lots. The oil so treated is stirred with water and diluted, whereby the aminophenol separates in a flocculent state and is filtered off. Each lot gives about 170 kilos. of the crude substance. The filtrate from the aminophenol and the mother liquors (after the sodium sulphate has crystallised out) are extracted with ether. All these liquors yield 30–35 kilos. of the aminophenol. The crude material is melted in portions of 250 kilos. in enamelled pans, about 50 kilos. of toluene are added and the whole is allowed to crystallise. About 140 kilos. of the pure aminophenol are obtained from each crystallisation.

The filtrates and washings are distilled to recover the toluene. The residue, consisting of tarry aminophenol, is stirred with water and then with an insufficient quantity of hydrochloric acid so that sparingly soluble impurities will not be dissolved. The solution so obtained is clarified by the slow addition of sodium carbonate solution and well stirred. The clear solution, which must now give a pure white precipitate on adding sodium carbonate solution, is filtered into enamelled pans and then treated again with sodium carbonate. If the material which separates out remains oily in spite of continual stirring, it is scooped out and a further quantity of the aminophenol is precipitated. If the product now separates in white flocks the precipitation can be carried further. It can be considered as finished if the colour of the precipitate changes or if the product is no longer soluble in ether.

Further addition of sodium carbonate precipitates only inorganic impurities. When the aminophenol has settled to the bottom, the clear liquor is siphoned off and the residue filtered and dried in a centrifuge.

The treatment of the aminophenol with acid is done in casks. The residue from this treatment is also mixed with water and an insufficient amount of hydrochloric acid to dissolve it. The solution obtained, after being clarified, is then treated as described above. This treatment of the residues is continued until no more pure aminophenol is obtained by the use of cold hydrochloric acid. The various oily fractions are treated in a separate cask with acid and sodium carbonate in the same way. The residues in the casks are then united, sufficient water and very little acid added, and the whole is boiled by means of steam for half an hour. After cooling, the liquid is clarified and treated as above, the first two fractions being kept separate. This treatment of the residue is continued until it becomes hard and brittle. The first two fractions, mentioned above, are later purified in a similar way. The purified product is finally crystallised.

The following plant is required for the manufacture. The sulphate is prepared in two enamelled pans (each 250 litres) which are fitted with stirrers and stand in a low, cooling tub. The fluid mixture, while still warm, is transferred by means of earthenware ladles to stoneware jars and thence to the sulphonating pan. This is a closed pan of 850 litres capacity and is furnished with an agitator. The lid is fitted with a small manhole cover, connexion with compressed air, a thermometer pipe, and a blow-out pipe. The pan is built into an oven (2 : 1·7 : 1·7 metres) arranged with a small fireplace. A flue for the acid fumes, steps to the oven, scales, and a blow-out pipe complete the fittings. The fuming sulphuric acid is warmed and melted in a special stove heated with steam.

The liming of the sulphonation is carried out in a rectangular vessel (1·2 : 1·6 : 2·4 metres) of 4,600 litres capacity. The open end of the pipe connected to the blow-out pipe of the sulphonation pan terminates in a corner of the vessel about 0·5 metre from the side. A water tap is fixed above the vessel and a footstep placed at the side so that the contents can be conveniently stirred by hand. The quicklime required is slaked and sieved in a different place. The lime is spread out in a layer and slaked by means of a watering can. The larger and unattacked pieces are raked out and again watered. The slaked lime is left for a day and then sieved in a mechanically driven sieve. The sieved material is transported in large boxes fitted with handles or piled up in a container (about 2,000 litres). The sodium carbonate is dissolved in a cask into which water and steam can be brought.

The mixture, after being treated with sodium carbonate, is pumped through a 10-chambered filter press with water and compressed air connexions. The filtered solution and the first wash-water run into a shallow rectangular vessel (1·9 : 0·4 : 0·8 metres); the succeeding wash-waters flow into a lower container (0·8 : 0·8 : 1·6 metres) of about 1,000 litres capacity.

The calcium sulphate from the press is emptied into two shallow boxes and thrown away. For filtering half a sulphonation mixture, the press has to be filled eleven times. The solutions are sent to the evaporating pans by means of two centrifugal hand-pumps.

The evaporators consist of a large pan (4·6 : 1·5 : 0·4 metres) of about 2,700 litres capacity and a deeper one (2·5 : 1·5 : 1 metres) of about 1,800 litres capacity. The latter is fixed over the fire, whilst the former is heated by the gases coming from this. The flow of liquor from one pan to the other goes on automatically by means of a siphon.

When the liquors from one operation are sufficiently concentrated, the requisite quantity of sodium hydroxide is dissolved in them and the solution evaporated until the mass has become thick and no longer foams. During this last evaporation the mass is stirred by hand with an iron stirrer. When this point is reached, the fire is shut off and the contents of the pan are ladled out and poured, by means of a gutter, into two smaller pans (1·9 : 0·9 : 0·5 metres), each of 500 litres capacity, the material being equally divided between them. In these pans the mass is strongly heated and dried until the temperature has risen to 160–170°, the whole being stirred during the operation. The mixture is now dug out with spades and transferred to shallow trays, where it is allowed to cool. It is then broken up and preserved in casks with well-fitting covers.

The melting is done in a large oven (5·8 : 2 : 0·5 metres), which is furnished with two fireboxes and forms an air-bath. The top has twenty circular openings in which the tubes containing the above mixture can be hung, by means of the rims at their upper ends. These tubes are closed by means of two covers clamped on. The top cover carries a short tube to allow the steam to escape. Each pair of tubes is raised to the top of the oven by means of a pulley which then travels horizontally along rails so as to bring the tubes vertically above the holes in the top of the oven, into which they are lowered.

The tubes are filled by means of a funnel. Forty tubes are required (20 cm. in diameter and 1·5 metres long), the oven being charged afresh as soon as the tubes are taken out.

The melt is dissolved in a long, narrow, high vessel (5·8 : 0·5 : 2 metres) of 5,500 litres capacity carrying crossbars to hold the tubes. In the lower part of this vessel is a stirrer protected, by means of a perforated false bottom, from any large pieces of the melt that might fall on it. The vessel is furnished with a water-supply, a steam pipe, and an outlet tap. When the tubes are cold and the covers removed, they are transported to the dissolving vessel and hung in it, and their contents dissolved by the hot water in the vessel. The emptying and cleaning of the tubes are hastened by means of an iron scraper. The water in the vessel is sufficient to dissolve the contents of 120 tubes.

Acidification of the solution is brought about in a strong cast iron pan (2·5 : 1·4 : 0·5 metres) of 1,750 litres capacity which is sunk in the ground and covered with a wooden lid. One half of this is loose, whilst the other half is fitted with a flue connected with the chimney, and has openings through which are run the solution and acid. The sulphuric acid is siphoned in from a lead-lined cask. A perforated steam-pipe is arranged in the pan, and the liquid is stirred by hand. After the treatment with acid the whole is allowed to settle and the clear liquor pumped off, whilst the residue is filtered and washed on the filter with hot water.

The treatment of the acid solution with sodium carbonate is carried out in a lead-lined, semi-circular vessel (1·8 : 1·1 metres) of 2,000 litres capacity. The separated aminophenol is filtered in a 10-chamber filter press. The filtrate runs into two tubs, each of 1,800 litres capacity, from which the solutions flow by gravity to the shallow reservoir (2,000 litres) in the ether-extraction room.

The mother liquors, after the crystallisation of the aminophenol, are pumped to the above tubs, from which they also flow to the ether-extraction plant. The extractor has a capacity of 400 litres.

For the purification of the crude aminophenol are required three crystallising pans, each of 250 litres capacity, a water-bath (made from a cask), three vessels (200 litres capacity) for the fractional precipitation of the aminophenol solution, three casks for dissolving the tarry products, four filter boxes, and other small appliances such as acid jugs, etc. The crystals are washed on a vacuum filter (0·7 metre diameter), centrifuged, and spread on 15–20 trays, covered with paper, so that they can be dried in the air. A still of 300 litres capacity is required for the toluene solutions.

The work is arranged as follows :

1*st Day.*—The sulphate for one operation is prepared, which can be done by a workman in seven to eight hours. When finished, it is transferred to the sulphonation pan. Also 800 kilos. of quicklime have to be slaked (four hours) and drums of fuming sulphuric acid to be placed in the stove.

2*nd Day.*—The sulphonation is carried out ; the slaked lime is sieved (six to eight hours), and in the course of the afternoon the milk of lime for the neutralisation is prepared (two workmen, three-quarters of an hour).

3*rd Day.*—Half of the sulphonation mixture is blown into the milk of lime (1½ hours). When this is neutralised, the sodium carbonate solution is added, the mixture stirred for fifteen minutes, and then the filter press is filled (¼ hour), one workman stirring the mixture and three working the pump. Washing the cake in the press takes one hour, the amount of water necessary being 600 litres. Blowing out and drying the cake require twenty to twenty-five minutes, and emptying the press fifteen minutes. The press is filled again four times during the day and time can be saved by blowing it dry during meal-times. Heating and evaporating can also be started.

4th Day.—The press is filled five times and a further quantity of lime is slaked.

5th Day.—The rest of the mixture is filtered, milk of lime made, using for this purpose the last wash-waters, and the second half of the sulphonation is blown over. The press can be filled four times. Fresh sulphate is prepared, slaked lime sieved, and fuming sulphuric acid put in the stove.

6th Day.—A sulphonation is carried out and the press filled five times.

7th Day (*Sunday*).—The oven is heated and the evaporation kept going.

8th Day.—The two last fillings of the press from the first operation. The oven is charged with twenty tubes, for which six men are required. The foreman looks after charging the tubes, one man weighs out the charges, a second puts a layer of clay on the lids of the tubes so as to make a tight joint, a third helps the foreman to shut the tubes, two others look after the pulleys, etc., and place the tubes in the oven, and the fireman raises the temperature.

The charging of the oven takes 1½ hours. The necessary temperature of the air-bath (300°) is reached after four hours, and this is kept for 18 hours longer.

On this day also the first half of the second sulphonation is limed out and the press filled three times. The liquors from the first operation are now evaporated so far that they can be put into the deep evaporating pan and the liquor from the second operation can go into the larger pan after it has been cleaned out (four men, two hours). A drum of sodium hydroxide is broken up and the contents are stored in a closed iron vessel.

9th Day.—Twenty tubes are taken out of the oven and the same number placed in it. The press is filled four times. The sodium hydroxide is dissolved in the evaporated solution of the sulphonate. At 11 a.m. the mixture is filled into the small pans (½ hour); at 4.30 p.m. it can be taken out. For this two men are required to stir, two to empty the pans, one man removes the filled trays. At 2.30 p.m. the cooled tubes are opened and hung in the dissolving vessel (¾ hour), and at 5.30 p.m. they are removed. Since beginning the melting operation, the oven is heated at night, and this is looked after by the workman on the extraction plant, who must also clean the lids of the tubes.

10th Day.—The oven is charged, the mixture for these melts broken up (two men, three hours) and weighed, the press filled four times, sulphate prepared, and the second half of the second sulphonation limed out. The melts have also to be dissolved. On this day three workmen work two hours' overtime.

11th, 12th, and 13th Days.—Work is carried on as above.

15th Day.—In addition to the ordinary work on the sulphonation, the working up of the melts is begun. The suitable quantity of liquid is run into the pan (¼ hour) and then acid is added (one man, three hours). The mixture is heated by steam for three-quarters of an hour and then pumped (½ hour) into the lead-lined, semicircular vessel. The addition of sodium carbonate requires 2½ hours (two men); after settling for half an hour the mother liquors are siphoned off (½ hour) and pumped to the crystallising vessel where sodium sulphate crystallises out. The treatment of the oil with dry sodium carbonate lasts half an hour, and then the mixture is diluted with water (one hour).

16th Day.—A fresh lot of the solution of the melts is acidified and at the same time the precipitated aminophenol is filtered through the filter press. In the afternoon the cake is melted (three hours), and later the toluene is stirred in. At midday the extraction of the aminophenol liquors will have been started. The filling of the extractor takes fifteen minutes and the same time is required for stirring and settling. The separation of the layers and charging with fresh ether can be done in ten minutes. The liquors are extracted twice and then heated (¾ hour) to distil off the dissolved ether. The apparatus must be cooled (¼ hour) before re-charging. The whole work necessary in the extraction takes 2½ hours, and four extractions can be done in the day.

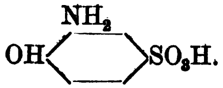
18th Day.—On this day the crystallisations are worked up. For removing and washing out the crystalline crusts half an hour is required, for breaking up, two hours, and for washing on the filter, two hours. The centrifuging requires half an hour for each 40–50 kilos. In the meantime, the mother liquors and wash-waters are distilled. Solution of the tarry aminophenol and clarification of the solution require half an hour, and the filtration one to two hours. The fractional precipitation takes half an hour and the removal of the clear solution and the filtration of the purified aminophenol require half an hour. What remains on the filter is centrifuged.

The whole manufacture requires one foreman and six workmen.

Diethyl-*m*-aminophenol melts at 78° and boils at 201°/25 mm., or 276–280° under atmospheric pressure.

It is used for the manufacture of Rhodamine B.

2-Aminophenol-4-sulphonic Acid,

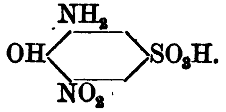


This acid is obtained (1) by nitrating phenol-*p*-sulphonic acid with half the amount of nitric acid as is used to prepare the dinitro-acid (below) and subsequent reduction with iron, (2) by sulphonating *o*-aminophenol, details of which are given below, and (3) by fusing aniline-2 : 5-disulphonic acid with sodium hydroxide.

The acid crystallises with $\frac{1}{2}H_2O$ and dissolves in 100 parts of water at 14°.

It is used for making Palatine chrome brown W, Acid alizarin garnet R, Acid alizarin violet N, and Diamond black PV.

2-Nitro-6-aminophenol-4-sulphonic Acid,



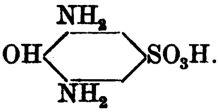
(1) Ten parts of phenol are heated with 13 parts of sulphuric acid at 100–110° for some time; the solution is cooled and poured into 100 parts of water; 40 parts of nitric acid (62 per cent.) are added, and the whole is heated to boiling until a sample, on cooling, deposits crystals of dinitrophenol. The solution is now allowed to cool, filtered from dinitrophenol, and 10 parts of potassium carbonate are added, when the potassium salt of dinitrophenolsulphonic acid separates in yellow crystals. Thirty parts of this are dissolved in 300 parts of hot water, the solution is cooled, and 200 parts of ammonium sulphide are added. The reduction proceeds with a slight rise in temperature and is complete in two to three hours. The acid can be precipitated by adding hydrochloric acid, or the solution is acidified with acetic acid and the potassium salt precipitated by adding potassium chloride. The potassium salt is sparingly soluble in cold, but more readily so in hot water (Badische Anilin- & Soda-Fabrik, E.P., 14252 of 1898; F.P., 280031; G.P., 121427; U.S.P., 644233).

(2) One hundred parts of *o*-aminophenol are dissolved in 480 parts of sulphuric acid and then 240 parts of fuming sulphuric

acid (containing 24 per cent. of sulphur trioxide) are added and the mixture is warmed for one hour to 90–95°. It is then cooled to 0° and a mixture of 58 parts of nitric acid and 116 parts of sulphuric acid is run in slowly at 0–3°. After the mixed acid has been added the whole is poured on ice after two hours. After four hours, the precipitate is filtered off, pressed, and dissolved in 400 parts of boiling water. The nitroaminophenolsulphonic acid crystallises, on cooling, in grey, shining prisms which are sparingly soluble in cold water (Society of Chemical Industry in Basle, G.P., 93443; U.S.P., 644233).

2-Nitro-6-aminophenol-4-sulphonic acid is used for making Vigoureux blacks.

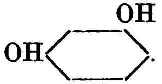
2 : 6-DIAMINOPHENOL-4-SULPHONIC ACID,



A solution of sodium 2 : 6-dinitrophenol-4-sulphonate (p. 129) is reduced by means of zinc dust and hydrochloric acid, and may be used direct for making azo-dyes (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 18624 of 1900; F.P., 310597; G.P., 148212; U.S.P., 680283).

It is used for making Palatine chrome blacks F, FN, FT, and S (Acid alizarin blacks SE and SN).

RESORCINOL,



This is manufactured by fusing benzene-*m*-disulphonic acid with sodium hydroxide. The following process is given by Bindschedler and Busch (*Mon. Sci.*, 1878, 1169).

*Preparation of Benzene-*m*-disulphonic Acid.**—Ninety kilos.

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* The sulphonation of benzene by pure concentrated sulphuric acid at 240–250° results almost exclusively in the formation of the *m*-disulphonic acid, less than 1 per cent. of the *p*-isomeride being produced after 1½ hours' heating. The addition of a little mercury causes the formation of the *m*- and *p*-acids in the proportion 2 : 1; ferrous sulphate acts similarly, about 10 per cent. of the *p*-disulphonic acid being produced (Behrend and Mertelsmann, *Annalen*, 1911, **378**, 352). The action of other catalysts, which have scarcely any influence on the reaction, has been studied by Mohrmann (*Annalen*, 1915, **410**, 373).

In sulphonating benzenesulphonic acid either with fuming sulphuric acid or with 98 per cent. acid, Polak (*Rec. trav. chim.*, 1910, **14**, 416) found that complete sulphonation to disulphonic acid takes place at 209°, whilst at 233° some trisulphonic acid is formed.

of fuming sulphuric acid are placed in a cast iron pan fitted with a stirrer and reflux condenser made of a leaden coil, and 24 kilos. of benzene are added in a thin stream through the condenser. The temperature gradually rises to the boiling point of benzene, and after two to three hours the latter is converted into the monosulphonic acid. The reflux condenser is then shut off and the pan connected with an ordinary condenser. The temperature is now raised gradually to 275°, and water and a little benzene distil over.* After heating for about twenty minutes at this temperature, the mass is allowed to cool, blown into 2,000 litres of water, neutralised with milk of lime, and converted into the sodium salt in the usual way, the solution of the salt being subsequently evaporated to dryness.†

Fusion.—Sixty kilos. of this product are added to 150 kilos. of sodium hydroxide previously melted with the addition of a little water and the mass is heated at 270° in a cast iron pan with continual stirring for eight to nine hours, during which time it becomes almost solid. On cooling, it is dissolved in about 500 litres of boiling water, the solution acidified with hydrochloric or sulphuric acid, and boiled to expel the sulphur dioxide. A little tarry matter separates out and, after the solution is cool, this is filtered off and the filtrate thoroughly extracted with ether in a copper extraction apparatus. This is a sloping cylinder fitted with a stirrer, of about 250 litres capacity. It is completely filled with the liquid and a very slow stream of ether is passed through while stirring. The ether becomes saturated with resorcinol and the solution is distilled, the ether being used over again. The liquid in the extraction apparatus is treated continuously with ether until no more resorcinol is contained in it. For each 5 kilos. of resorcinol, 1 kilo. of ether, or 1 per cent. of the amount used, is lost.

The resorcinol remains as an almost colourless liquid which crystallises on cooling. It is heated in an enamelled pan to 215° to expel the last traces of ether and water. The residue contains about 92–94 per cent. of resorcinol. This is distilled, when water and phenol pass over first and then pure resorcinol. An almost theoretical yield is obtained.

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* The Barrett Co. (U.S.P., 1279295, 1279296) distils off the water below 260° under diminished pressure.

† Dennis (U.S.P., 1227252) proposes to treat the mixture of benzenedisulphonic acid and sulphuric acid with benzene, which dissolves the sulphonic acid but not the sulphuric acid, and to treat the solution with a suitable compound to form a salt of the sulphonic acid, which is relatively insoluble in the benzene.

The following description of the manufacture on a larger scale is given by Mühlhäuser (*Dingl. Polyt. J.*, 1887, **263**, 154).

The plant required is as follows :

For the Preparation of the Monosulphonic Acid.—A cast iron jacketed pan of 400 litres capacity fitted with stirrer and a lead reflux condenser. Steam and water are connected to the jacket.

For the Preparation of the Disulphonic Acid.—A cast iron jacketed pan of 800 litres capacity fitted with stirrer and an ordinary lead condenser. The jacket is filled with oil and heated by fire.

A tub (3,000 litres) with stirrer, for liming the acid mixture, connected with an egg (3,000 litres) and an 18-chamber filter press. A shallow, cast iron pan (6,000 litres), fitted with two steam coils, one above the other, for evaporating the filtered solution. A tub (3,000 litres) for making the sodium salt connected with an egg (3,000 litres) and a 6-chamber filter press. Two evaporating pans with stirrers (each 1,500 litres). Two drying pans, 150 cm. in diameter and 30 cm. deep. Grinding mill.

For the Melt.—A cast iron pan (600 litres) with stirrer, heated by direct fire.

For Acidification.—An earthenware vessel (1,500 litres) fitted with a lid carrying two funnels for adding acid and a flue to the chimney. A lead-lined egg (1,500 litres).

For the Extraction.—The extraction apparatus consists of a closed vessel (2,000 litres) fitted with a stirrer, a separator (2,000 litres), and a container (500 litres) for the amyl alcohol. Also a steam-jacketed still (1,200 litres) carrying a dome and a steam-pipe reaching to the bottom, and a condenser.

For the Purification.—An enamelled drying pan, a copper vacuum still (75 litres) fitted with a thermometer and heated by direct fire, a copper Liebig's condenser, and a receiver fitted with a vacuum gauge.

Preparation of Benzenemonosulphonic Acid.—Three hundred kilos. of sulphuric acid (67° Bé.) and 60 kilos. of pure benzene are placed in the sulphonation pan, the mixture well stirred and warmed to about 80°. The pipe between the reflux condenser and the pan should feel only slightly warm to the hand. The process is carried on for ten hours, when the monosulphonation should be complete.

Preparation of Benzenedisulphonic Acid.—Next day the above batch is blown over into the larger sulphonation pan, 85 kilos. of dry, ground sodium sulphate are added, the stirrer is kept going, and the oil-bath heated to 240°. After about four hours, the contents of the pan will have reached a temperature of about 225°, and are kept at this point for about eight hours. During the first period of heating benzene distils over and sulphur dioxide is evolved.

Conversion into Sodium Salt.—On the following day, the contents of the pan are blown into 1,500 litres of water contained in the tub and neutralised with slaked lime made from 200 kilos. of quicklime. (The slaked lime should be run into the tub through a sieve.) In order to render the gypsum easy filterable, about 800 litres of cold water are added to the boiling mixture, which is then run down into the egg and passed into the 18-chamber filter press. The filtrate runs into the large evaporating pan and the press-cake is again boiled up with about 1,500 litres of water, cold water added as before, and again filtered. The united filtrates are evaporated to about 2,000 litres and then run into the tub, where 6–10 kilos. of sodium carbonate are added to convert the calcium salt into the sodium salt. The mixture is run into the egg and the calcium carbonate collected in the 6-chamber filter press. The filtrate is evaporated in the two evaporating pans until it is thick enough to stop the stirrers. The moist salt is then completely dried in the drying pans, being continually stirred with an iron rake, and the dry powder is ground and sieved. The yield is 200 kilos. The following table shows the result of two batches :

Sulphuric acid.	Benzene.	Sulphate.	Lime.	Soda.	Benzene recovered.	Yield.
300	60	85	200	6·5	14	180
300	60	85	210	9·0	8	200

Melt.—Two hundred and fifty kilos. of solid sodium hydroxide are put in the melt pan, 10 kilos. of water added, and the coke fire is lit. The sodium hydroxide gradually melts and a skin is formed on the surface. Heating is continued until no skin is formed and until the crusts forming on the side of the pan are also melted. If now some of the sodium salt is thrown into the sodium hydroxide and it dissolves rapidly with a hissing noise, the alkali is sufficiently hot. The stirrer is started and 125 kilos. of the dry sodium salt are added within about half an hour, care being taken that the mass does not foam over. This can be regulated by stopping and starting the stirrer. The foaming gradually ceases and the melt acquires an oily appearance ; it becomes yellow and then brown. When no further reaction appears to be taking place, the mass is scooped out on to iron trays, where it solidifies on cooling.

Acidification.—The broken up cakes are put into the earthenware vessel, to which 500 litres of water have been added, and 7–8 carboys of concentrated hydrochloric acid are poured in until the sulphur dioxide is driven off and the solution shows an acid reaction to litmus.

Extraction.—The solution is run down into the lead-lined egg and blown to the extraction apparatus, where it is extracted four times with amyl alcohol, 100 litres being used for each extraction. The solution and amyl alcohol are mixed together for about thirty minutes, and then blown to the separator, which is a cylinder with a pointed end. After settling for an hour, the aqueous solution is run back into the extractor and the amyl-alcoholic solution of resorcinol to the container.

The aqueous solution, after being treated four times with the alcohol, is completely extracted and the fourth extract is scarcely coloured. The united extracts are allowed to remain for twelve hours, any aqueous liquor which has settled out is drawn off, and the alcoholic solution run to the still.

Distillation with Steam.—The solution of resorcinol is first heated to about 100° with indirect steam and then steam is passed into the still to drive over the amyl alcohol. When only water emerges from the condenser, the resorcinol solution is run into the enamelled drying pan, where the water is evaporated, the operation taking about twelve hours.

Purification.—The resorcinol is purified by distillation in a vacuum. The contents of the drying pan (about 30 litres) are run into the vacuum still and the latter is closed. The Liebig's condenser leads the distillate to a copper receiver fitted with a tap at the bottom, which in its turn is connected with the vacuum pump. On heating, a little water and phenol pass over, and these are run out of the receiver through the tap at the bottom. At about 190°, this tap is shut and the pressure is reduced by 630 mm. On further heating, the resorcinol begins to boil and distils over into the receiver. Care must be taken that the condenser is not stopped up. The liquid resorcinol is run into tinned copper moulds. About 20–23 kilos. of pure resorcinol are obtained from 125 kilos. of the disulphonate. Two batches gave:

Sodium hydroxide.	Benzenedisulphonate.	Hydrochloric acid.	Amyl alcohol.	Crude resorcinol.	Pure resorcinol.
250	125	720	400	28	19
250	125	740	400	29	23

Schoop (*Zeitsch. Chem. Ind.*, 1887, 2, 1) also gives a description of the manufacture of resorcinol which differs only in a few respects from the foregoing. These points only will therefore be noted, whilst the illustrations from Schoop's paper are reproduced.

The monosulphonation is performed in the pan *K* (Fig. 18), 650 kilos. of sulphuric acid and then 130 kilos. of benzene being added to it through the funnel *t*. For the disulphonation the mass is blown by compressed air (*a*) into two pans (*D*). Each of these, therefore, receives 390 kilos. of the mixture and, in addition, 92 kilos. of dry sodium sulphate are added.

Schoop remarks that after four hours' heating at 225° the sulphonation mixture becomes solid. The addition of more sulphuric acid would, however, counteract this. He uses 12 kilos. of sodium carbonate to convert the calcium salt into the sodium salt, obtaining 410–420 kilos. of the dry sodium benzenedisulphonate, and about 16 kilos. of benzene are recovered.

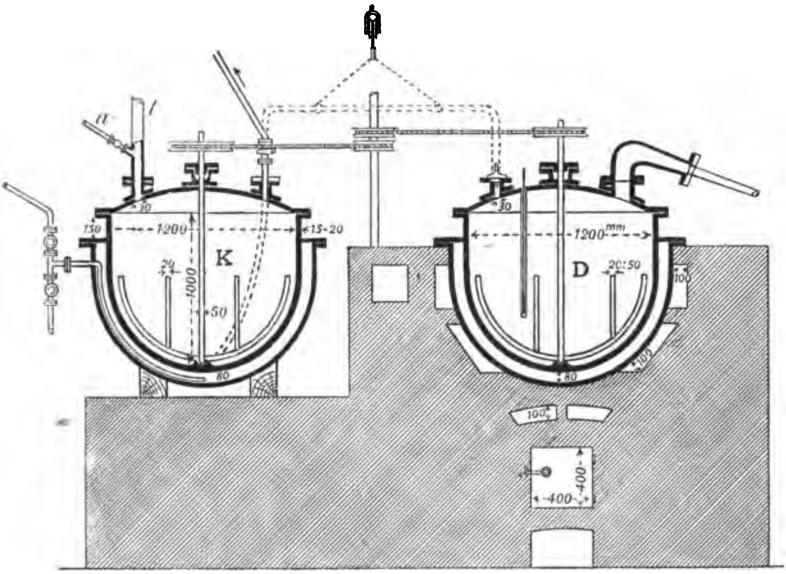


FIG. 18.

The neutralisation is effected in a tub of about 5,500 litres capacity, and the egg into which the limed mixture is run has a capacity of about 2,000 litres. The solution of calcium salt is immediately (before evaporation) converted into the sodium salt in a tub of 3,500 litres capacity. One drying pan is used, 1·5 metres in diameter and 1 metre deep.

The press-cake of gypsum is boiled twice with water, 500 litres being used each time. This wash-water, instead of being added to the main filtrate and evaporated, is used for dissolving the next sulphonation.

For the melt, 250 kilos. of sodium hydroxide and 125 kilos. of the dry sodium salt are used. The melting of the sodium hydroxide takes about 2½ hours and the addition of the salt about half an hour.

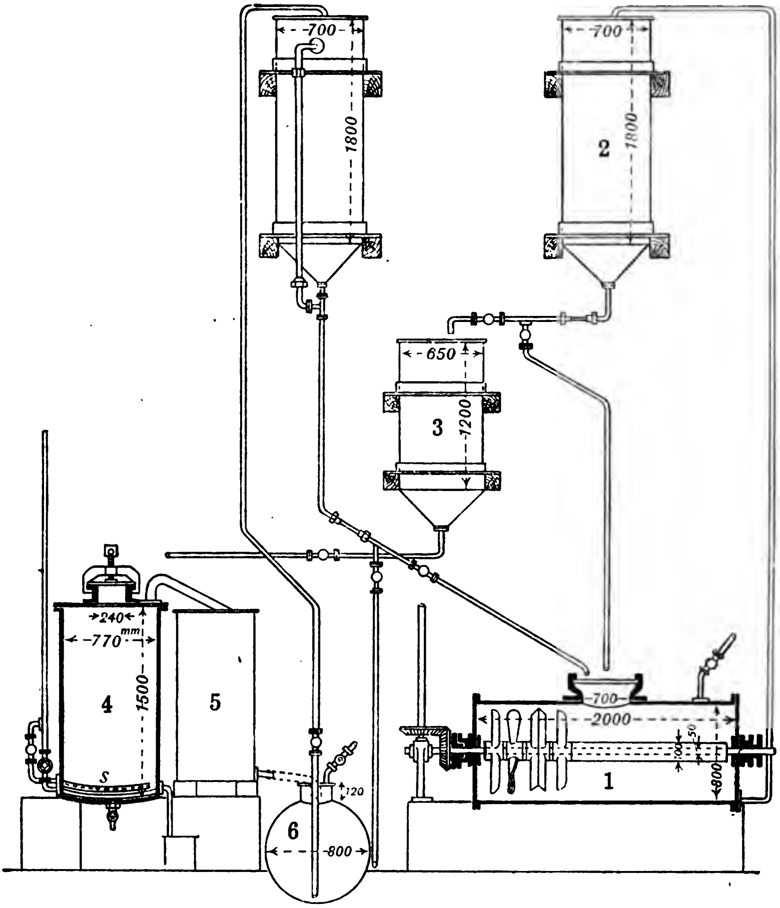


FIG. 19.

The acidification of the melt is done in two earthenware pots, each of 300 litres capacity. The amount of amyl alcohol used for each of the four extractions is 75 kilos. and each extraction takes one hour. In Fig. 19 the extractor is indicated by 1, the separator by 2, and the container for the alcoholic extract by 3.

The still (4), condenser (5), and egg (6) for collecting the volatilised amyl alcohol are also shown. The still used is lined with lead, and is fitted with copper coils (*s*) through which steam is passed in order to raise the contents to boiling point.

The vacuum still *A* (Fig. 20) has a capacity of about 150 litres and is connected with a copper condenser *B* and through this with an enamelled cast iron receiver *C* fitted with a heating coil *s*. The pipe *n* leads to the vacuum pump.

The yield from one operation is 60 kilos. of crude, or 48–50 kilos. of rectified, resorcinol. The first runnings of the vacuum distillation, from several operations, are collected and, on redistillation, yield a further quantity of resorcinol.

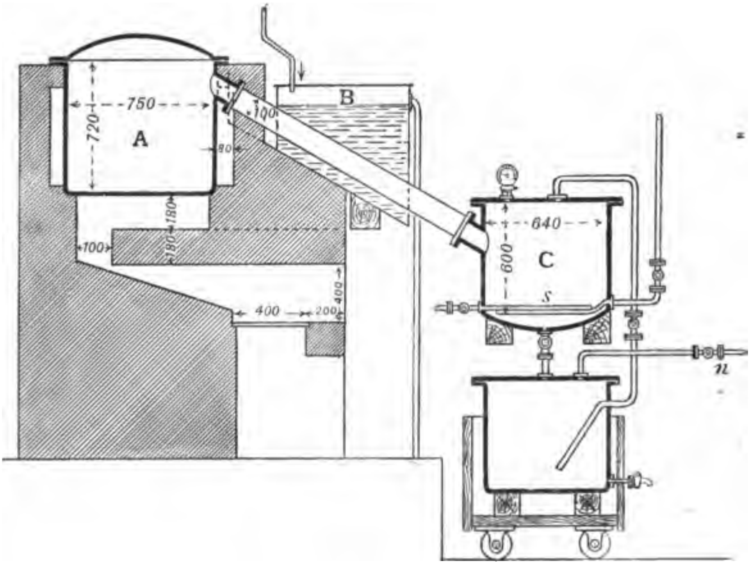


FIG. 20.

Note.—The theoretical yield from 125 kilos. of sodium benzenedisulphonate, if the latter is anhydrous, is 48·7 kilos. of resorcinol. The salt crystallises with $4H_2O$ and it is possible that this is not all driven off on drying. It would appear that Schoop put two charges of crude resorcinol into his still, particularly as this had twice the capacity of that used by Mühlhäuser. He would thus get, from 125 kilos. of the sodium salt, 30 kilos. of crude, or 24–25 kilos. of pure, resorcinol, which would agree with Mühlhäuser's figures.

Resorcinol should give a clear solution in water, and the solution should remain clear on the addition of lead acetate (precipitation of catechol).

If an odour of benzoquinone is perceived on warming with ferric chloride, quinol is probably present. The aqueous solution of resorcinol should not give a red colour with a pine splinter. When an ethereal solution is shaken with a few drops of concentrated sodium hydroxide solution, any phenol present is preferentially dissolved and on acidifying the alkaline solution the odour of phenol is perceived.

Resorcinol melts at 119°, boils at 276·5°, and is volatile with steam. One hundred parts of water dissolve 86·4 parts at 0°, 147 parts at 12·5°, and 228·6 parts at 30°.

It is used for making Fast green (dinitrosoresorcinol), Fluorescein and the dyes derived from it, Sudan G, Resorcine yellow, Acid alizarin garnet R, Resorcine brown, Fast brown, Pyramidol brown BG and T, Congo 4R, Isodiphenyl black R, Coomassie union blacks, Congo brown G (Direct brown GR), Congo brown R, Azocorinth, and Hessian brown BBN.

Aldehydes and their Derivatives.

Benzaldehyde, CHO.

Benzaldehyde was formerly prepared by heating benzylidene chloride with milk of lime under a pressure of 5 atmospheres, the benzaldehyde being then distilled over with steam and the benzoic acid, which is also formed, being recovered from the calcium benzoate by acidification.

According to Espenschied (G.P., 47187), the reaction takes place under the ordinary pressure if chalk or barium sulphate is added along with the milk of lime, so as to emulsify the benzylidene chloride. The process now adopted, however, is that due to Schultze (G.P., 82927, 85493).

Sixty kilos. of the crude benzylidene chloride are heated by indirect steam to 20–25°, 20 grams of powdered iron are added, and then 10–15 kilos. of water. The vessel is then connected with an arrangement for absorbing the hydrogen chloride and the temperature raised to 90–95°. The reaction is regulated by the rate at which the hydrogen chloride can be condensed. When the evolution of the gas has ceased, the contents of the vessel are made alkaline by means of milk of lime prepared from 9–10 kilos. of quicklime, and the benzaldehyde is distilled over by means of steam. The residue is filtered and decomposed by hydrochloric acid, when the benzoic acid is obtained.

For certain purposes, the benzaldehyde, after being separated from the water, must be purified, and this is effected through the sodium hydrogen sulphite compound. Two hundred kilos. of the crude aldehyde (D 1·050–1·056), together with 1,000 kilos. of sodium hydrogen sulphite solution (25–30° Bé.), are placed in a vessel fitted with an agitator and steam coil. The mixture is stirred and heated slowly to 40° so as to bring about the dissolution of the benzaldehyde. When this is effected, the solution is allowed to settle, whereby impurities fall to the bottom, and the liquid is filtered into an autoclave, milk of lime added, and the mixture heated for some time to decompose the sodium hydrogen sulphite compound. The benzaldehyde is then distilled in a current of steam, separated from water, and rectified. One hundred and sixty kilos. of crude benzylidene chloride, 25 kilos. of lime, and 350 kilos. of sodium hydrogen sulphite solution give 60 kilos. of benzaldehyde, 20 kilos. of benzoic acid, and 300 kilos. of hydrochloric acid (20° Bé.) (Grandmougin, *Rev. prod. chim.*, 1917, **20**, 297).

Another method of preparing benzaldehyde consists in oxidising toluene with manganese dioxide in sulphuric acid solution (Société Chimique des Usines du Rhône, E.P., 22121 of 1897; F.P., 276258; G.P., 101221, 107722; U.S.P., 613460). Three hundred kilos. of toluene and 700 kilos. of sulphuric acid (65 per cent.) are placed in a pan furnished with an agitator, the mixture is thoroughly well stirred, and 90 kilos. of finely divided manganese dioxide (recovered) are added gradually. The temperature is kept at 40°, and when the oxidation is finished, the benzaldehyde and excess of toluene are distilled over with steam. The toluene (250 kilos.) and benzaldehyde (50 kilos.) can be separated by treatment with sodium hydrogen sulphite solution as described above or by treatment with sulphurous acid (Chemische Fabrik Griesheim-Elektron, G.P., 154499) as follows: Forty kilos. of the aldehyde are treated with 400 litres of water and 25–30 kilos. of sulphur dioxide at 15°; the aldehyde dissolves and the solution, after separation, is heated to 100°. The sulphur dioxide which is evolved is condensed and used again, whilst the benzaldehyde is separated from the aqueous liquor. Allowing for the toluene recovered, 100 kilos. of toluene, 250 kilos. of manganese dioxide, 2,000 kilos. of sulphuric acid (65 per cent.), and 75 kilos. of liquid sulphur dioxide give 100 kilos. of benzaldehyde (Grandmougin, *loc. cit.*).

The following brief mention may be made of other methods for the manufacture of benzaldehyde which have been patented.

Benzyl chloride is converted into benzaldehyde by treating it with concentrated sulphuric acid (Jenssen, E.P., 889 of 1879; F.P., 129220; G.P., 6685).

Schmidt (G.P., 20909) chlorinates boiling toluene until it attains a specific gravity of 1·175, when it consists essentially of a mixture of two molecular proportions of benzyl chloride with one molecular proportion of benzylidene chloride. This is boiled with six times its volume of water and a quantity of manganese dioxide containing 2 atoms of available oxygen to the above molecular proportion. The reaction is considered to take place according to the equation,

$$2C_6H_5\cdot CH_2Cl + C_6H_5\cdot CHCl_2 + 2MnO_2 = 3C_6H_5\cdot CHO + 2MnCl_2 + H_2O.$$

The product is distilled in a current of steam to obtain the benzaldehyde.

Benzaldehyde is also produced by heating benzylidene chloride with sodium acetate and a little zinc acetate (Jacobsen, E.P., 2878 of 1880; F.P., 137419; G.P., 11494, 13127).

Another method consists in oxidising benzylaniline to benzylideneaniline, which, on the addition of acids, decomposes into benzaldehyde and aniline. The two operations are combined by adding a mixture of sodium dichromate and sulphuric acid to a boiling mixture of benzylaniline and water; or benzylideneanilinesulphonic acid, prepared by oxidising benzylanilinesulphonic acid, is treated with a solution of aniline hydrochloride, whereby benzylideneaniline is precipitated and sulphanilic acid remains in solution (as its sodium salt). The benzylidene compound is then decomposed by stirring it in the cold with the equivalent quantity of a dilute mineral acid, which causes the benzaldehyde to separate, whilst the aniline remains in solution and is used again (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 10689 of 1896, 30118 of 1897; G.P., 110173).

It has been proposed to prepare benzaldehyde from benzene by submitting it, at 40–50°, to the combined action of carbon monoxide and hydrogen chloride in the presence of cuprous chloride and aluminium chloride (Farbenfabriken vorm. F. Bayer & Co., E.P., 13709 of 1897; G.P., 126421), or by treating it, at 30–40°, with a mixture of hydrocyanic acid and hydrogen chloride in the presence of aluminium chloride (*idem*, E.P., 19204 of 1897; F.P., 270334; G.P., 99568).

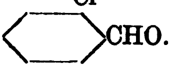
From toluene, it can be obtained by oxidation (1) with nickel oxide (Badische Anilin- & Soda-Fabrik, E.P., 22887 of 1900; F.P., 306071; G.P., 127388; U.S.P., 698355; compare also Woog, *Compt. rend.*, 1907, **145**, 124); (2) with ferric oxide (Chavy, Delage, and Woog, F.P., 379715); (3) with cerium oxide (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 19178 of 1902; F.P., 328069; G.P., 158609; U.S.P., 757136); (4) with vanadium pentoxide (The Selden Co. and Gibbs, E.P., 119517 [1917]); (5) with manganese dioxide sulphate, MnO_2,SO_3 (Badische Anilin- & Soda-Fabrik, E.P., 17982 of 1903; G.P., 175295), or (6) with lead dioxide and sulphuric acid (Chemische Fabrik Griesheim-Elektron, G.P., 154499).

Another method consists in boiling a solution of 14 kilos. of hexamethylenetetramine in 400 litres of 60 per cent. alcohol with 12·5 kilos. of benzyl chloride for five to six hours; 200 litres of water are added, the alcohol is distilled off, and the benzaldehyde driven over with steam. The benzaldehyde, after purification by means of sodium hydrogen sulphite, weighs 7·5–9 kilos. Alternatively, 12·5 kilos. of benzyl chloride are stirred into a solution of 14 kilos. of hexamethylenetetramine in 600 litres of water, the solution is heated for two hours, and the benzaldehyde obtained as above (Fabriques de Produits de Chimie organique de Laire, G.P., 268786).

Benzaldehyde boils at 179°/760 mm., 112·5°/100 mm., 76°/15 mm., or 62°/10 mm., and solidifies at −13·5°. It has D_4^{15} 1·0504 and dissolves in 300 parts of water.

It is used for making *m*-nitrobenzaldehyde and Malachite green, Brilliant green, Guinea green B, Light green SF, Acridine orange R extra, and Benzoflavine.

o-CHLOROBENZALDEHYDE,



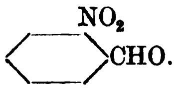
When *o*-nitrotoluene is treated with a stream of chlorine at 120–140° until about one-half of the theoretical amount of chlorine has been absorbed (see under Chlorobenzene, p. 6), a mixture of *o*-nitrobenzyl chloride and *o*-chlorobenzyl chloride is produced, the liquid containing about 40 per cent. of the chlorides together with excess of *o*-nitrotoluene. The former are hydrolysed and separated in the following manner.

Six hundred kilos. of the chlorinated *o*-nitrotoluene are boiled under a reflux condenser with 800 litres of dilute alcohol, 250 kilos. of crystallised sodium acetate, and 90 kilos. of sodium carbonate until the benzyl acetates are hydrolysed. The alcohol is distilled off,* and then steam is passed in to drive over the *o*-nitrotoluene (see below). The residue is diluted with water, if necessary, to retain the sodium acetate and chloride in solution, and, on cooling, the benzyl alcohol derivatives solidify and are filtered off and pressed. One hundred and thirty kilos. of the press-cake are dissolved in 400–500 kilos. of sulphuric acid (50–60° Bé.) at 40° and a mixture of sulphuric and nitric acids (70–80 kilos. containing 38–39 per cent. of HNO_3), or the corresponding quantity of nitric acid or sodium nitrate, is slowly added. Nitrous gases are evolved, and the temperature is kept at 40° during the oxidation. When the process is finished, as shown by the cessation of the evolution of nitrous fumes, the solution is run into 500 litres of water, the aldehydes are separated from the acid, and washed free from acid with water and, finally, with sodium carbonate solution. The mixture of aldehydes is filtered and pressed. From the pressed out oil the *o*-chlorobenzaldehyde is obtained by fractional distillation in a current of steam. The press-cake of *o*-nitrobenzaldehyde is sufficiently pure for technical purposes, but it can be purified by treatment with sodium hydrogen sulphite or by distillation with steam to remove the last traces of the *o*-chloro-derivative. Alternatively, the *o*-nitrotoluene need not be distilled off with steam, but the product of oxidation may be treated with sodium hydrogen sulphite solution, which dissolves the aldehydes and the *o*-nitrotoluene can easily be separated from the solution. The aldehydes are liberated by means of sodium hydroxide and separated as described above (Kalle & Co., E.P., 11259 and 11260 of 1898; F.P., 278102; G.P., 111010; U.S.P., 673887; compare also G.P., 104360, 115516).

Its preparation from *o*-chlorotoluene, through *o*-chlorobenzylidene chloride, has been described by Erdmann (*Annalen*, 1893, **272**, 141, 151), and by oxidation with manganese dioxide by the Société Chimique des Usines du Rhône (E.P., 22121 of 1897; F.P., 276258; G.P., 101221; U.S.P., 613460).

o-Chlorobenzaldehyde melts at —4°, boils at 213–214°, and has D^{8} 1·29. It is used for making Night green A (Neptune green SG), Setoglaucine O, and Setocyanine O.

o-NITROBENZALDEHYDE,



This is obtained in the nitration of benzaldehyde (to the extent

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* For the isolation at this point of *o*-nitrobenzaldehyde, see p. 143.

of about 20–25 per cent.: see under *m*-Nitrobenzaldehyde, p. 144), and also from *o*-nitrobenzyl chloride (see under *o*-Chlorobenzaldehyde, p. 141).

Another method of isolation, from the product obtained after distilling off the alcohol from the mixture of *o*-nitro- and *o*-chlorobenzyl alcohols (see asterisk, p. 142), is to add water to dissolve the sodium salts and to separate the mixture of oils. These are stirred for a short time with 1,000 kilos. of sulphuric acid (56° Bé.), the mixture is allowed to settle, the sulphuric acid solution of *o*-nitrobenzyl alcohol drawn off from the undissolved nitrotoluene, etc., and oxidised direct to *o*-nitrobenzaldehyde.

Alternatively, the oily mixture, without separating the nitrotoluene, is added to 600 kilos. of sulphuric acid (55° Bé.) and oxidised at 35–40° with nitric acid or a mixture of nitric and sulphuric acids. The product is run into 600 kilos. of ice-water, the oil separated, neutralised with sodium carbonate solution, and extracted with 400 kilos. of sodium hydrogen sulphite solution (40 per cent.) and 200 kilos. of water, at 30–40°, the whole being well stirred; 800 litres of water are added to dissolve the partly separated bisulphite compound, the mixture is allowed to settle, and the nitrotoluene drawn off. The bisulphite solution is precipitated by adding dilute sodium hydroxide solution and the free aldehyde filtered, pressed, and dried (Kalle & Co., E.P., 11259 of 1898; G.P., 106712).

Fischer (E.P., 15179 of 1888; F.P., 193686; G.P., 48722) heats *o*-nitrobenzyl chloride with alcohol and sodium acetate to obtain the acetate, and oxidises this with lead peroxide.

It can also be prepared by the oxidation of *o*-nitrobenzylaniline or its sulphonic acid to the corresponding *o*-nitrobenzylidene derivative and hydrolysis of the latter with acid (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 10686 of 1896, 15890 and 30118 of 1897; F.P., 258051, 273423; G.P., 91503, 92084, 93539, 97847, 97948; U.S.P., 575237, 622854, 636994), and by oxidising *o*-nitrotoluene with manganese dioxide (Société Chimique des Usines du Rhône, E.P., 22121 of 1897; F.P., 276288; G.P., 101221; U.S.P., 613460; Badische Anilin- & Soda-Fabrik, E.P., 21947 of 1899; G.P. Anm. B., 25232) or with nickel oxide (*idem*, E.P., 22887 of 1900; F.P., 306071; G.P., 127388; U.S.P., 698355), or the dimercuric compound,

$$NO_2{\cdot}C_6H_4{\cdot}CH{<}\begin{matrix}Hg\\Hg\end{matrix}{>}O,$$

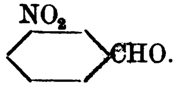
of *o*-nitrotoluene with potassium nitrate and sulphuric acid

(Kalle & Co., E.P., 22336 of 1906; F.P., 370522; G.P., 182218, 186881), or by treating the dinitrite of this dimercuric compound with hydrochloric acid (*idem*, G.P., 199147).

When *o*-nitrotoluene is oxidised by nitric acid under certain conditions, *o*-nitrophenylnitromethane is formed, which on mild oxidation yields *o*-nitrobenzaldehyde. Two thousand kilos. of *o*-nitrotoluene are heated to 110–120° and 1,000 kilos. of nitric acid (70 per cent.) are added gradually and regularly during eight hours, the temperature being kept at 110–120°. The water and excess of nitric acid distil off and are condensed. The *o*-nitrobenzoic acid and *o*-nitrobenzaldehyde which are formed are extracted respectively with sodium carbonate and sodium hydrogen sulphite and the *o*-nitrophenylnitromethane is then separated from the excess of *o*-nitrotoluene by prolonged extraction with sodium hydroxide solution, the latter being then treated with carbon dioxide to liberate the *o*-nitrophenylnitromethane. The yield of this is 200–250 kilos. (Société Chimique des Usines du Rhône, E.P., 6076 of 1911; G.P., 239953), but a yield of 400–500 kilos. is obtained if 1,000 kilos. of nitric acid (100 per cent.) are passed in the form of vapour into the *o*-nitrotoluene, heated to 140°, in about three hours, the temperature being maintained at 130–140° (*idem*, E.P., 17985 of 1911; G.P., 246381). On oxidising the substance with a neutral or weakly alkaline solution of permanganate, it yields *o*-nitrobenzaldehyde (*idem*, E.P., 24872 of 1910; F.P., 421922; G.P., 237358; U.S.P., 997301).

o-Nitrobenzaldehyde melts at 46° and boils at 153°/23 mm. It is used for making Indigo salt T.

m-NITROBENZALDEHYDE,



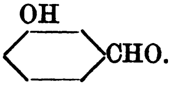
The product of the nitration of benzaldehyde consists of about 80 per cent. of the *m*- and 20 per cent. of the *o*-nitro-derivative.

According to Friedländer and Henriques (*Ber.*, 1881, **14**, 2802), benzaldehyde is slowly added to a cooled solution of rather more than the calculated amount of sodium nitrate in concentrated sulphuric acid, the temperature not being allowed to rise above 30–35°. On pouring the product on ice, the *m*-compound solidifies and is separated from the oily *o*-compound by pressing. The above authors obtained 100–105 grams of *m*-nitrobenzaldehyde and about 25 grams of oily *o*-nitrobenzaldehyde from 100 grams of benzaldehyde.

Ehrlich (*Ber.*, 1882, **15**, 2009) added 100 grams of benzaldehyde very slowly and carefully to 110 grams of nitric acid mixed with sulphuric acid, the temperature not being allowed to rise above 5°. The best yield of *m*-nitrobenzaldehyde is stated to be 95 per cent.

m-Nitrobenzaldehyde melts at 58° and boils at 164°/23 mm. It is used for making Patent blue V (Acid blue G), Patent blue A (Neptune blue B, Brilliant acid blue A), and Fast green.

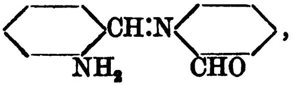
m-HYDROXYBENZALDEHYDE,



This is prepared by the diazo-reaction from *m*-aminobenzaldehyde.

Preparation of m-*Aminobenzaldehyde.*—(1) Six hundred and eighty kilos. of ferrous sulphate are dissolved in 2,000 litres of water and 250 kilos. of calcium carbonate paste are added. The mixture is boiled and a solution of 60 kilos. of *m*-nitrobenzaldehyde in 120 kilos. of sodium hydrogen sulphite solution (30 per cent.) and 500 litres of water gradually run in. Carbon dioxide is evolved and the nitro-compound at once reduced. The whole is filtered, the solution acidified and boiled to expel sulphur dioxide, and the solution of *m*-aminobenzaldehyde is employed direct (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 11049 of 1891; F.P., 214516; G.P., 62950, 66241).

(2) 2·19 Parts of crude nitrobenzaldehyde, containing about 25 per cent. of the ortho-compound, are heated to boiling with 10 parts of sodium hyposulphite (hydrosulphite) and 100 parts of water. After ten minutes, the solution is cooled to 50° and hydrochloric acid, corresponding with the sum of both bases, is added. The solution is boiled to expel sulphur dioxide and, on cooling, the anhydro-derivative of *o*-aminobenzaldehyde,



crystallises out quantitatively. This is filtered off and the solution of *m*-aminobenzaldehyde hydrochloride used direct. Oxalic or sulphuric acid may be used instead of hydrochloric acid (Farbenfabriken vorm. F. Bayer & Co., E.P., 22398 of 1909; F.P., 408184; G.P., 218364).

Conversion of m-*Aminobenzaldehyde into* m-*Hydroxybenzaldehyde.*—To the solution of *m*-aminobenzaldehyde sufficient hydrochloric acid is added to ensure the presence of rather more than 2 molecules of acid to 1 molecule of the base. The solution is cooled to 0°, diazotised by running in a concentrated solution of 1 molecular proportion of sodium nitrite, and then heated with direct steam until the evolution of nitrogen has ceased. The *m*-hydroxybenzaldehyde is isolated by evaporating the solution to the crystallising point or extracting it with ether or benzene.

m-Hydroxybenzaldehyde melts at 107° and boils at 240° and 160–161°/20 mm. It is readily soluble in water, alcohol, ether, or benzene, but insoluble in light petroleum. It is used for making Cyanol extra.

BENZALDEHYDE-*o*-SULPHONIC ACID,

Fifty litres of sodium hydrogen sulphite solution (40 per cent.), diluted with 150 litres of water, are neutralised exactly with sodium hydroxide and heated with 20 kilos. of *o*-chlorobenzaldehyde for eight hours at 170–180° (temperature of oil-bath =190–200°). The pressure need not be more than 8 atmospheres. The contents of the autoclave are treated with 13 kilos. of sulphuric acid and boiled to expel sulphur dioxide and traces of *o*-chlorobenzaldehyde. The liquid is cooled, filtered from a little *o*-chlorobenzoic acid, neutralised with sodium carbonate, evaporated to dryness, and the sodium salt extracted with alcohol. On evaporation of the alcohol, the sodium salt is obtained as a powder very readily soluble in water. Instead of evaporating the solution of the sodium salt to dryness, the rather sparingly soluble barium salt may be prepared and the solution evaporated to crystallisation (Geigy & Co., E.P., 5068 of 1896; F.P., 254742; G.P., 88952).

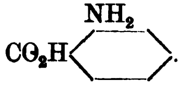
The acid is a syrup, and the sodium and barium salts crystallise in long prisms (Gnehm and Schüle, *Annalen*, 1898, **299**, 347).

The acid can also be obtained by oxidising stilbenedisulphonic acid (prepared by eliminating the amino-groups from diaminostilbenedisulphonic acid) with potassium permanganate (Levinstein, E.P., 21968 of 1897; G.P., 119163), but the process does not appear to be used on the large scale.

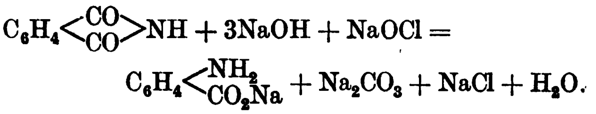
Benzaldehyde-*o*-sulphonic acid is used for making Erioglaucines.

CARBOXYLIC ACIDS AND THEIR DERIVATIVES.

ANTHRANILIC ACID,



This is prepared from phthalimide by the action of sodium hypochlorite :



$$C_6H_4 < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > NH + 3NaOH + NaOCl =$$
$$C_6H_4 < \begin{smallmatrix} NH_2 \\ CO_2Na \end{smallmatrix} + Na_2CO_3 + NaCl + H_2O.$$

Preparation of Phthalimide.—Six hundred and fifty parts of phthalic anhydride are melted in a cast iron pan heated by gas and gradually brought to 140° in the course of four hours. The temperature is then gradually raised to 170° during the next seven or eight hours. At the end of this period, the temperature is raised to 240°. The pan has an arrangement by which gaseous ammonia can be introduced. The ammonia is led into the molten phthalic anhydride from pressure cylinders and the current of gas can be observed and regulated by causing it to pass through two Woulfe's bottles half filled with water; 70–75 parts of ammonia are required and the whole operation from start to finish lasts eighteen hours. The product (635 parts) is run into a pan, cooled, broken up, and ground (H. Levinstein, *J. Soc. Dyers,* 1901, **17**, 139).

Phthalimide melts at 228°.

Anthranilic Acid.—Five hundred parts of phthalimide are dissolved in a cold solution of 144 parts of chlorine in 640 parts of sodium hydroxide solution (40° Bé.) and 440 parts of water. The solution is filtered and then blown into a tub fitted with a stirrer, and saturated with sulphur dioxide. Anthranilic acid separates on the addition of about 600 parts of hydrochloric acid (H. Levinstein, *loc. cit.*; Amsterdamsche Chinine-fabrik, E.P., 18246 of 1890; Badische Anilin- & Soda-Fabrik, G.P., 55988).

The acid is also obtained by oxidising aceto-*o*-toluidide with permanganate in the presence of magnesium sulphate and hydrolysing the product (Badische Anilin- & Soda-Fabrik, E.P., 6475 of 1897; G.P., 94629; Chemische Fabrik von Goldenberg, Geromont & Co., G.P., 119462).

Five kilos. of aceto-*o*-toluidide and 10·33 kilos. of crystallised magnesium sulphate are heated with 600 litres of water, in an enamelled pan fitted with a stirrer and set in a water-bath, to 75–80° until a clear solution is obtained, and then 14·6 kilos. of crystallised potassium permanganate are added all at once. The temperature rises to 85° and is kept at that point until the permanganate has disappeared (about 1½ hours). The hot solution is filtered, the filtrate concentrated, and acidified with dilute sulphuric acid. The acetylanthranilic acid is collected and hydrolysed by heating with sodium hydroxide solution.

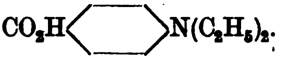
Another process consists in boiling a mixture of 137 kilos. of *o*-nitrotoluene, 120 kilos. of sodium hydroxide, and 500 kilos. of alcohol under reflux until the odour of nitrotoluene has disappeared. The solution is then saturated with ammonia and hydrogen sulphide and boiled for several hours until reduction to anthranilic acid is complete. The solution is evaporated to dryness to expel alcohol and excess of ammonium sulphide, and the residue dissolved in water, filtered, and the anthranilic acid precipitated by adding acid to the filtrate (*idem*, E.P., 18319 of 1899; F.P., 292468; G.P., 114839; U.S.P., 661821).

Phthalylhydroxylamine yields anthranilic acid when boiled with sodium carbonate (Basle Chemical Works, G.P., 130301, 130302), as does also phthalylhydroxamic acid (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 1982 of 1902; F.P., 318050; G.P., 136788).

When phthalimide is oxidised in alcoholic solution, anthranilic ester is obtained (Basle Chemical Works, G.P., 139218).

Anthranilic acid is readily soluble in water or alcohol, and melts at 144·6°. It is used for making 2-hydroxythionaphthen, phenylglycine-*o*-carboxylic acid, and Indanthrene violet RN.

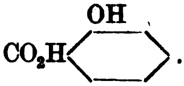
p-Diethylaminobenzoic Acid,



Carbonyl chloride (phosgene) is passed into diethylaniline at the ordinary temperature until it ceases to be absorbed. The crystalline mass thus obtained is melted and again treated with the gas until no more is absorbed. The product is mixed with water and the excess of diethylaniline removed by acetic acid. After filtration, the colouring matter is separated by washing with alcohol, and the residue crystallised from alcohol. The acid can also be prepared by ethylating *p*-aminobenzoic acid (Michler and Gradmann, *Ber.*, 1876, **9**, 1912).

It melts at 188°, and when gently warmed (5 kilos.) with phosphorus pentachloride (4·9 kilos.) it is converted into the chloride (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 4961 of 1884; F.P., 181351; G.P., 34463; U.S.P., 35266), which is not isolated, but used direct for making Acid violet 7B.

SALICYLIC ACID,



Powdered sodium hydroxide is dissolved in a small quantity of water and the necessary amount of phenol, either solid or liquid, is added with stirring, when it quickly dissolves. The solution is evaporated in the autoclave in which the salicylic acid is made; the operation is performed in a vacuum and the mass of sodium phenoxide must be well stirred. In order to remove the last traces of water, the mass is heated to 150–160°, but must be cooled to 100° before the carbon dioxide is introduced, and during this cooling the stirrer must be in operation and the vacuum maintained. The heating and cooling are best effected by tubes fitted inside the autoclave. Dry carbon dioxide (1 mol. to 1 mol. of phenol) is introduced slowly, the temperature not being allowed to exceed 145°, and the pressure inside the autoclave is kept at about 6 atmospheres, so that, if the gas is contained in a cylinder, it must pass through a reducing valve. The contents of the autoclave are dissolved in water and the diluted solution is warmed with stannous chloride solution (Hofmann, G.P., 65131) until the liquid is colourless. The tin is precipitated as $SnO(OH)_2$, the filtered solution precipitated with hydrochloric acid and the salicylic acid filtered off, centrifuged and washed with water (Schmitt, *Dingl. Polyt. J.*, 1885, **255**, 259; Heyden, E.P., 10167 of 1884; F.P., 163161; G. P., 29939; U.S.P., 334290; E.P., 7801 of 1886; addition to F.P., 163161; G.P., 38742. The mechanism of the reaction is discussed by de Bruyn and Tymstra, *Rec. trav. chim.*, 1904, **23**, 385; Tymstra, *Ber.*, 1905, **38**, 1375; 1912, **45**, 2837; Moll van Charante, *Proc. K. Akad. Wetensch. Amsterdam*, 1906, **9**, 20; *Rec. trav. chim.*, 1908, **27**, 58, and Sluiter, *Ber.*, 1912, **45**, 59, 3008).

The acid can be obtained in a snow-white condition by distillation with superheated steam (Rautert, *Ber.*, 1875, **8**, 537) or by sublimation.

Marasse (E.P., 17002 of 1893; F.P., 232352; G.P., 73279, 78708) heats an intimate mixture of phenol and 3 parts of potassium carbonate at 130–160° and treats it with carbon dioxide. The reaction proceeds according to the equation:

$$2C_6H_5\cdot OH + K_2CO_3 + CO_2 = H_2O + 2C_6H_4(OH)\cdot CO_2K.$$

The excess of potassium carbonate may be replaced by kieselguhr (Aktiengesellschaft für Anilinfabrikation, G.P., 76441), but neither process is employed on the large scale.

Schering (E.P., 274 of 1901; F.P., 307186; G.P., 133500; U.S.P., 757702) substitutes the product obtained by the fusion of sodium benzenesulphonate (200 kilos.) with sodium hydroxide (111 kilos.) for the sodium phenoxide in Heyden's process.

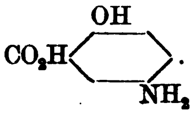
Salicylic acid melts at 158·5°. Its solubility in water at various temperatures is shown in the table below, the figures opposite the temperatures being grams of acid in 1,000 grams of solution (Savarro, *Atti R. Accad. Sci. Torino*, 1913, **48**, 455).

0°	1·24	35°	3·51	70°	13·70
5	1·29	40	4·16	75	17·55
10	1·35	45	4·89	80	22·09
15	1·84	50	6·38	85	27·92
20	2·00	55	7·44	90	37·35
25	2·48	60	9·00	95	50·48
30	2·98	65	10·94	100	75·07

It dissolves in 172 parts of benzene at 18·2° and is readily soluble in acetone, alcohol, or ether. The sodium salt is very readily soluble in water or alcohol.

Salicylic acid is used for making Alizarin yellow FS, GG, and R, (Mordant yellow 3R), Chrome fast yellow GG, Diamond flavine G, Eriochrome phosphine R, Mordant yellow O (Alizarol yellow, Anthracene yellow BN, Salicin yellow D), Crumpsall yellow, Oriol yellow, Diamond yellow G, Anthracene acid brown, Azoalizarin Bordeaux W, Azoalizarin black I, Anthracene yellow C, Benzo fast yellow 5GL, Hessian yellow, Chrysamine, Dianol fast red F (Direct fast red F, Diamine fast red F), Direct brown 3RB (Diamine brown M), Oxamine red, Crumpsall browns, Anthracene red, Diamine yellow N, Benzo olive, Benzo grey, Diamine bronze, Trisulphone browns, Columbia black green D, Eboli green, Diphenyl greens, Dianol green G (Erie direct green, Diamine green G), Columbia green, Chrome violet, and Direct brown GR (Naphthamine brown 4G).

AMINOSALICYLIC ACID,



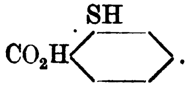
This can be obtained by reducing the corresponding nitrosalicylic acid (Beilstein, *Annalen*, 1864, **130**, 243; Hübner, *ibid.*, 1879, **195**, 18; Hirsch, *Ber.*, 1900, **33**, 3239; compare also Deninger, *J. pr. Chem.*, 1890, [ii], **42**, 550), or by the electrolysis of a solution of *m*-nitrobenzoic acid in sulphuric acid (Gattermann, *Ber.*, 1893, **26**, 1850; Farbenfabriken vorm. F. Bayer & Co., G.P., 77806), or by treating a solution of *m*-nitrobenzoic acid in sulphuric acid with zinc dust (Farbwerke vorm. Meister, Lucius, & Brüning, G.P., 96853), but no doubt the best method of manufacture is to reduce the azo-dye, benzeneazosalicylic acid. The reduction with sodium hyposulphite (hydrosulphite) is carried out as follows : A mixture of 500 grams of aniline hydrochloride, 600 grams of hydrochloric acid (D 1·19), and 3,000 grams of ice, which shows a temperature of —20°, is diazotised by the addition of a solution of 290 grams of sodium nitrite in 1 litre of water. [On the large scale aniline and not the hydrochloride would be used and dissolved in 2½ molecular proportions of hydrochloric acid.] The diazonium chloride, after fifteen minutes, is run into a solution of 533 grams of salicylic acid in 2,200 grams of crystallised sodium carbonate [= 815 grams of anhydrous carbonate] and 10 litres of water. The yellow sodium salt of the azo-compound separates out and is filtered off and washed with a little water (Fischer and Schaar-Rosenberg, *Ber.*, 1899, **32**, 81 ; these authors reduce the azo-compound with stannous chloride and hydrochloric acid).

The paste of azo-compound is now boiled with about 10 litres of water, rendered alkaline with sodium hydroxide solution, and dry sodium hyposulphite added until reduction is evidently complete. About 1,350 grams of hyposulphite are required. The aniline produced is distilled off with steam and the solution of aminosalicylic acid (sodium salt) used direct for making azo-dyes (Grandmougin, *Ber.*, 1906, **39**, 3930 ; *J. pr. Chem.*, 1907, [ii], **76**, 127).

The reduction can also be effected by means of zinc dust and ammonia or ferrous sulphate and sodium carbonate.

Aminosalicylic acid decomposes at 280° and is sparingly soluble in water. The sodium salt is readily soluble. It is used for making Era black F (Fast chrome black B, Diamond black F, Chrome fast blacks), Diamond greens, Anthracene acid blacks, Chrome Bordeaux, and Sulphanil black C.

THIOSALICYLIC ACID,



(*o*-THIOLBENZOIC ACID).

(1) Fifty kilos. of *o*-chlorobenzoic acid are stirred with a little water in an iron pan and converted into the sodium salt by the addition of 38·5 kilos. of sodium hydroxide solution (40° Bé.). One hundred kilos. of potassium hydrogen sulphide and a solution of 0·2–0·5 kilo. of copper sulphate, or finely-divided

copper, are added, and the mixture is heated very gradually to 150–200°. When most of the water has been driven off, the mass becomes dark red and melts. On raising the temperature to about 250°, the mass becomes viscous, the temperature rises, and the mass gradually solidifies. It is then dissolved in 1,000 litres of water, the solution filtered, and the filtrate acidified, when a quantitative yield of thiosalicylic acid is obtained (Cassella & Co., G.P., 189200).

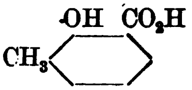
The operation can also be performed in an autoclave; thus 200 kilos. of crystallised sodium sulphide are melted in an autoclave and evaporated until the temperature is 125–130°. Fifty kilos. of sodium *o*-chlorobenzoic acid are then stirred in, and the autoclave is closed and heated for six to ten hours at 200°. The product is dissolved in hot water, the solution filtered and acidified, when thiosalicylic acid is obtained, accompanied by a little dithiosalicylic acid, which is easily reduced to the former by means of zinc and hydrochloric acid. The addition of a small amount of copper or of copper salts to the melt is of advantage (*idem*, G.P., 193290).

(2) One hundred and thirty-seven kilos. of anthranilic acid are stirred with 500 litres of water and 240 kilos. of concentrated hydrochloric acid, ice is added, and diazotisation effected by running in a concentrated aqueous solution of 69 kilos. of sodium nitrite. The diazo-solution is run into a solution, cooled with 300 kilos. of ice, of 33·6 kilos. of sulphur and 260 kilos. of sodium sulphide in 260 litres of water to which has been added 130 kilos. of sodium hydroxide solution (40° Bé.). The temperature is so regulated during the addition that it does not exceed 5°. Nitrogen is evolved and the temperature rises rapidly to 15–25°. After some hours, hydrochloric acid is added until the mixture is acid, when it is filtered and washed with 1,000 litres of water. The residue is dissolved by boiling it with 60 kilos. of sodium carbonate and water, the solution filtered from sulphur, and heated to boiling with the addition of 60–100 kilos. of ground iron or the corresponding amount of zinc dust for some hours, until a sample, treated with sodium hydroxide and then filtered, gives, on acidifying, no odour of hydrogen sulphide and a precipitate which is easily soluble in cold alcohol. The mass is then treated with 120 kilos. of sodium hydroxide solution (40° Bé.), and again boiled up and filtered. By precipitating the filtrate with hydrochloric acid, thiosalicylic acid is obtained as a colourless to pale yellow crystalline precipitate, which, after cooling, is filtered and washed (Kalle & Co., G.P., 205450).

The reduction of dithiosalicylic acid (30 grams) can also be effected by warming it with grape sugar (21 grams), water (100 c.c.) and sodium hydroxide (24 grams) for ten minutes on the water-bath (Claasz, *Ber.*, 1912, **45**, 2427).

Thiosalicylic acid melts at 164–165° and is used for making phenylthioglycol-*o*-carboxylic acid.

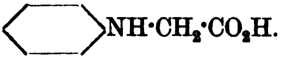
o-Cresotic Acid,



This is prepared by the same methods as are employed in the manufacture of salicylic acid, using *o*-cresol instead of phenol.

It resembles salicylic acid in its properties and melts at 163–164°. It is used for making Toluylene orange G (Direct orange Y) and Cresotine yellow G and R.

Phenylglycine,



Phenylglycine is prepared (1) by the action of chloroacetic acid on aniline, and (2) by the action of hydrocyanic acid and formaldehyde on aniline and hydrolysis of the nitrile thus obtained. By the first method there is a tendency for 2 molecules of acid to condense with 1 molecule of aniline, so that a salt or an ester of the acid is used, or an excess of aniline is employed.

The following are the chief methods that have been described.

(1) One hundred parts of chloroacetic acid, 300 parts of aniline, and 200 parts of dilute alcohol are boiled for two hours in a digester fitted with a stirrer and reflux condenser. The product is rendered alkaline with sodium hydroxide and the alcohol and aniline are driven over with steam. After cooling, 120 parts of hydrochloric acid (30 per cent.) are added to precipitate the phenylglycine, of which 36–38 parts are obtained from every 25 parts of aniline entering into the reaction (Chemische Fabrik von Heyden, E.P., 14049 of 1902; F.P., 322536; G.P., Anm., H. 26908).

(2) A mixture of 95 grams (1 mol.) of chloroacetic acid, 186 grams (2 mols.) of aniline, and 500 c.c. of water is heated on the water-bath for 1½ hours, shaking frequently, the hot liquid is poured into a dish, and the crystalline product collected and washed with cold water until free from hydrochloric acid. The yield varies between 105 and 120 grams, that is, between 70 and 80 per cent. of the theoretical. When prepared in this way, the product contains a small proportion of phenylglycino-acetic acid (de Mouilpied, *Trans.*, 1905, **87**, 438).

(3) Friswell (E.P., 18149 of 1907; G.P., 177491) employs the sodium salt of the acid and gives an example of the preparation of *o*-tolylglycine, for which an almost theoretical yield is claimed. One hundred and seven grams of *o*-toluidine, 116·5 grams of sodium chloroacetate, and 150 c.c. of water are heated under reflux for three to four hours. On cooling, *o*-tolylglycine separates as a yellowish cake.

(4) A mixture of 100 kilos. of chloroacetic acid and 500 kilos. of aniline is heated to 100° for three hours. The temperature is then raised to 120° and the mixture heated in a vacuum as long as water distils. Sodium carbonate is now added and the aniline distilled in a current of steam. On cooling, phenylglycineanilide crystallises out. This is collected and heated with aqueous sodium hydroxide (1 mol. to 1 mol. of the anilide) in an autoclave. The aniline is distilled off by means of steam and the solution evaporated to dryness in a vacuum. Alternatively, a solution of 100 kilos. of chloroacetic acid in 200 litres of water is added to 500 kilos. of aniline and the mixture heated under reflux for three hours. The water is then distilled off under diminished pressure; in the course of the distillation, the temperature is raised to 120–140° and kept at this point until no more water passes over. Sodium hydroxide solution is now added, the aqueous layer separated from the aniline layer, and the latter mixed with sodium hydroxide solution (1 mol.) and heated in an autoclave fitted with a stirrer to about 140°. The aniline is then distilled in a current of steam and the solution of the sodium salt of phenylglycine evaporated to dryness (Badische Anilin- & Soda-Fabrik, E.P., 5564 of 1905; F.P., 352311; G.P., 169358; U.S.P., 818341).

(5) Five hundred parts of aniline are heated with 100 parts of chloroacetic acid for two hours at 120°; 61 parts of sodium carbonate are added, the sodium chloride is filtered off and washed with aniline, and the oily filtrate converted into potassium phenylglycine by heating with 110 parts of a 50 per cent. solution of potassium hydroxide to 130–150° for one to two hours under a pressure of 2–3 atmospheres (Chemische Fabrik Griesheim-Elektron, E.P., 3980 of 1911; F.P., 426123; U.S.P., 1011500).

(6) Six hundred and twenty kilos. of nitrobenzene, 1,000 kilos. of finely-divided cast iron, and 70 kilos. of aniline are introduced into a vessel provided with an agitator, reflux condenser, and thermometer. The whole is heated to about 70°, whereupon a solution of 470 kilos. of monochloroacetic acid in 1,000 litres of

water is gradually run in. The chloroacetic acid is added in such a manner that the mass may remain boiling. The heating is continued for another couple of hours at 98–100°, and the mass is then neutralised with a concentrated solution of 600 kilos. of sodium carbonate, and distilled with steam, about 70 kilos. of aniline passing over, which can be used again. The mixture is passed through a filter press and the residue washed with water. The phenylglycine is separated from the combined filtrate and washings, after being concentrated to about 3,000 litres, by the addition of the requisite quantity of a mineral acid (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 9700 of 1906; F.P., 374948; G.P., 175797; U.S.P., 841456).

(7) Four hundred parts of aniline, with or without water, are heated to 80–90° in a pan fitted with a stirrer and reflux condenser, and then a solution of 200 parts of chloroacetic acid in about 100 parts of water and a hot solution of 100 parts of sodium carbonate in 350 parts of water are added slowly independently, and the addition is so regulated that a faintly acid reaction persists throughout. The whole is heated on the water-bath for a short time and the molten aniline salt of phenylglycine separated, or, if the mixture is allowed to cool, the crystalline mass is collected, after diluting with water if necessary, and washed with a little water. The aniline salt is then converted into phenylglycine in the usual way (Chemische Fabrik Weiler-ter-Meer, G.P., 244825).

(8) Ten kilos. of chloroacetic acid are dissolved in 10 litres of water, and 8 kilos. of calcium hydroxide, $Ca(OH)_2$, are added with cooling; a mixture of 10 litres of methyl or ethyl alcohol and 30 kilos. of aniline is then run in and the mixture stirred and warmed until the reaction is complete. The alcohol and aniline are distilled off with steam, and, on cooling, the sparingly soluble calcium salt is filtered off. It is converted into the sodium salt in the usual way, and phenylglycine is obtained from the concentrated solution of the latter by adding the calculated amount of a mineral acid (Wohl and Blank, G.P., 167698).

(9) One thousand two hundred and fifty kilos. of ferrous chloride are dissolved in water and precipitated with sodium hydroxide or sodium carbonate. To this 300 kilos. of salt are added and the mixture is heated to 90–100°. Four hundred and seventy-two kilos. of chloroacetic acid are run in, then 510 kilos. of aniline are quickly introduced, and the whole is heated for 1½ hours under reflux. On cooling, the iron salt of phenylglycine is collected, washed with cold water, stirred with water, and decomposed

with sodium carbonate or hydroxide. The mixture is heated to boiling and the uncombined aniline distilled off with steam. The solution is filtered from iron oxide or carbonate, and phenylglycine is precipitated from it by the cautious addition of a dilute mineral acid (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 9774 of 1906; F.P., 375055; G.P., 177491; U.S.P., 868294).

Instead of chloroacetic acid, its amyl ester may be condensed with aniline and the resulting amyl ester then hydrolysed (Lippmann, G.P., 163515), or the ethyl ester is condensed with aniline in the presence of calcium carbonate (Imbert and Consortium für Elektrochemische Industrie, G.P., 194884).

(10) A mixture of 140 kilos. of dichlorovinyl ether,*

$$C_2HCl_2{\cdot}O{\cdot}C_2H_5,$$

300 kilos. of aniline, and 100 litres of water is boiled for twenty-four hours, rendered alkaline and the excess of aniline distilled in a current of steam. The residue consists of 90 per cent. of phenylglycine ethyl ester and 10 per cent. of phenylglycine-anilide. Alternatively, 100 kilos. of aniline may be used instead of 300 kilos., and the mixture boiled until acid to Congo paper. The greater part (not more than nine-tenths) of the aniline hydrochloride formed is neutralised with chalk and the boiling continued. This operation is repeated until all the dichlorovinyl ether has disappeared, the reaction being complete in about twenty-four hours. The remaining aniline is driven over with steam, and the product consists of 80 per cent. of the ester and 20 per cent. of the anilide (Imbert and Consortium für Elektrochemische Industrie, E.P., 13176 of 1907; F.P., 379830; G.P., 199624; U.S.P., 894149).

(11) Seventy-five parts of formaldehyde (40 per cent.) are mixed with 50 parts of sodium cyanide (98 per cent.) in a pan fitted with an agitator and reflux condenser; 93 parts of aniline and sufficient alcohol or wood spirit to give a homogeneous liquid are added. The mixture is warmed on the water-bath, and, when once started, the reaction proceeds quickly, ammonia being evolved in accordance with the equation:

$$C_6H_5{\cdot}NH_2+CH_2O+NaCN+H_2O=C_6H_5{\cdot}NH{\cdot}CH_2{\cdot}CO_2Na+NH_3.$$

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* Prepared by boiling a mixture of 40 kilos. of sodium hydroxide, 100 kilos. of quicklime, and 131·5 kilos. of 94 per cent. alcohol for twelve hours, cooling, adding 131·5 kilos. of trichloroethylene at 60–65°, and raising the temperature to the boiling point. The dichlorovinyl ether is isolated by distillation or is distilled over with steam (Imbert and Consortium für Elektrochemische Industrie, E.P., 5014 of 1907; F.P., 375167; G.P., 216940; U.S.P., 894148).

When the evolution of ammonia has ceased, the alcohol is distilled off and the solution of the sodium salt of phenylglycine is evaporated to dryness. If alcohol is not used, an aqueous solution of the cyanide is added to the mixture of aniline and formaldehyde previously warmed to the temperature of the water-bath (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 22733 of 1901 ; F.P., 315940 ; G.P., 135332).

According to the Basle Chemical Works (G.P., 145376), the above process gives only a 60 per cent. yield of the theoretical. A yield of more than 90 per cent. of the theoretical is claimed when the reaction is carried out as follows. A mixture of 186 kilos. of aniline, 200 litres of alcohol, and 5 litres of sodium hydroxide solution (30 per cent.) is warmed with 80 kilos. of formaldehyde (37·9 per cent.) ; at the boiling point of the alcohol a previously warmed 49·3 per cent. potassium cyanide solution (132 litres) is run in. A vigorous reaction ensues, ammonia is evolved, and after warming for half an hour all is in solution. The alcohol is distilled off and then the aniline is driven over with steam, the remaining solution of phenylglycine being evaporated to dryness.

The nitrile of phenylglycine can be obtained by the action of formaldehyde on a mixture of aniline and an alcoholic solution of hydrocyanic acid (Miller, Plöchl, and Hofer, *Ber.*, 1892, **25**, 2028 ; Fabriques des Produits Chimiques de Thann et de Mulhouse, E.P., 24461 of 1902).

Phenylglycine may also be obtained from oxanilic acid, $C_6H_5·NH·CO·CO_2H$, by reduction with sodium amalgam or zinc dust (Koepp & Co., G.P., 64909 *) or by electrolytic reduction with lead cathodes (Kinzlberger, G.P., 163842 ; U.S.P., 798920 ; G.P., 210693).

Phenylglycine forms white crystals melting at 127°, moderately soluble in water, sparingly so in ether, but readily so in the usual organic solvents. It forms soluble alkali salts and a green, insoluble copper salt.

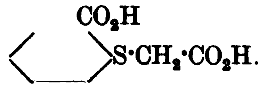
It is used for making Indigo.

o-Tolylglycine (p. 154) melts at 160° and is used for making Indigo MLB/T.

* Patent lapsed after one year.

Phenylthioglycol-*o*-carboxylic Acid,

(*o*-Carboxyphenylthioglycollic Acid ; *o*-Carboxyphenylthiolacetic Acid.)



(1) 15·4 kilos. of thiosalicylic acid are dissolved in water with the addition of 35 kilos. of sodium hydroxide solution (40° Bé.), 9·5 kilos. of chloroacetic acid are added, and the whole is gently heated. By the addition of acid, phenylthioglycol-*o*-carboxylic acid is precipitated in white crystals which are filtered off, washed, pressed and dried (Kalle & Co., E.P., 22736 of 1905 ; F.P., 359398 ; G.P., 192075 ; U.S.P., 850827). From a solution of thiosalicylic acid prepared from 30 grams of dithiosalicylic acid (p. 153) Claasz (*loc. cit.*) obtained 38–40 grams of phenylthioglycol-*o*-carboxylic acid, by warming it with a neutralised solution of 20 grams of chloroacetic acid in 100 c.c. of water.

(2) The diazo-compound obtained from 13·7 kilos. of anthranilic acid is combined with 10 kilos. of thioglycollic acid in slightly alkaline solution. As soon as the diazotised anthranilic acid has disappeared the product is precipitated by acidifying the solution, filtered, and redissolved in dilute sodium carbonate solution. The slightly alkaline solution is now heated gradually until it boils. As soon as the evolution of nitrogen has ceased, the solution is cooled and acidified with hydrochloric acid, when phenylthioglycol-*o*-carboxylic acid is precipitated (*idem, ibid.*).

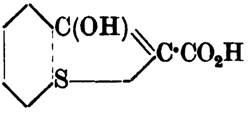
(3) Forty-six kilos. of anthranilic acid, dissolved in the necessary amount of water with the addition of 40 kilos. of hydrochloric acid, are diazotised in the usual manner with 23 kilos. of sodium nitrite, and the cold diazo-solution is run into a solution prepared from 11 kilos. of sulphur, 80 kilos. of crystallised sodium sulphide and a little water, the temperature being maintained at − 5° to +5° ; it should not rise above 10°. When the evolution of nitrogen has ceased, the solution is acidified and the benzoic acid derivative, mixed with sulphur, separates. It is dissolved in a cold solution of sodium carbonate, the solution filtered, and the filtrate mixed with a solution of 41 kilos. of sodium chloroacetate and 40 kilos. of sodium hydroxide solution (40° Bé.). The mixture is then heated to about 80°, filtered, and the filtrate acidified, when phenylthioglycol-*o*-carboxylic acid is precipitated (*idem*, E.P., 11174 of 1906 ; F.P., 366612 ; G.P., 181658).

A process very similar to the foregoing one is as follows : 137

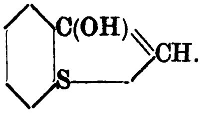
grams of anthranilic acid are diazotised by the aid of 200 grams of hydrochloric acid, 1,200 c.c. of water, and 70 grams of sodium nitrite; the solution is neutralised with sodium carbonate and allowed to flow gradually at about 0–10° into a solution of 240 grams of crystallised sodium sulphide in 500 c.c. of water, each portion of the diazo-solution being added only after the previous one has decomposed. A solution of 100 grams of chloroacetic acid in 100 c.c. of water and 114 grams of sodium hydroxide solution (40° Bé.) is now added and the mixture is heated on the water-bath until the reaction is complete. The phenylthioglycol-*o*-carboxylic acid is precipitated by adding hydrochloric acid (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 6930 of 1907; F.P., 385675; G.P., 199349; U.S.P., 877702). In an earlier patent by the same firm (E.P., 16580 of 1907[*]; F.P., 380053), diazotised anthranilic acid is treated with potassium ethyl xanthate and the *o*-xanthobenzoic acid is then condensed with chloroacetic acid.

Phenylthioglycol-*o*-carboxylic acid melts at 213° and is used for making hydroxythionaphthencarboxylic acid and hydroxythionaphthen.

2-HYDROXYTHIONAPHTHEN-1-CARBOXYLIC ACID[†] *and*
(THIOINDOXYLCARBOXYLIC ACID)
2-HYDROXYTHIONAPHTHEN
(THIOINDOXYL)



and



Twenty kilos. of phenylthioglycol-*o*-carboxylic acid are stirred with a little water and introduced, at 100°, into a mixture of 100 kilos. of sodium hydroxide and 20 litres of water. The

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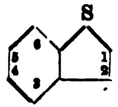
[*] Patent void; applied for by R. Lesser.

[†] In the German technical literature this compound is often referred to as 3-hydroxy(1)thionaphthen-2-carboxylic acid, and a certain amount of confusion has arisen through this arbitrary change from the rational numbering given by Richter ("Lexikon der Kohlenstoff-verbindungen," 3rd ed., I., p. 17), namely,



Benzthiofuran (thionaphthen),

which it does not seem necessary to alter.

temperature is then raised to 170–180° (the German patent gives 170–200°) and kept at that point for an hour. The product is dissolved in water and slightly acidified (care being taken that the temperature does not rise) with hydrochloric acid, and the precipitated 2-hydroxythionaphthen-1-carboxylic acid is filtered off, and pressed. If the acidified solution is warmed until the evolution of carbon dioxide ceases, 2-hydroxythionaphthen is produced, or 75 kilos. of a paste containing 20–23 per cent. of the carboxylic acid are diluted with 200 litres of water and heated with 10 kilos. of hydrochloric acid or submitted to the action of a current of steam. In the former case, the 2-hydroxythionaphthen separates out on cooling, and in the latter it distils over with the steam (Kalle & Co., E.P., 22736 of 1905; F.P., 359398; G.P., 192075; U.S.P., 850827. Compare Friedländer, *Ber.*, 1906, **39**, 1062).

Phenylthioglycol-*o*-carboxylic acid is also converted into hydroxythionaphthen by heating it with 3 parts of acetic anhydride to 90–110° or into the carboxylic acid if warmed to 40–50°; with 5 parts of acetic anhydride and 0·5 part of anhydrous sodium acetate short heating at 50–80° gives the carboxylic acid, whilst long heating results in the production of hydroxythionaphthen (Kalle & Co., E.P., 16101 of 1906; G.P., 198712; U.S.P., 850827).

Phenylthioglycol-*o*-carboxylic acid may also be heated alone at 230° until the evolution of gas ceases; part of the hydroxythionaphthen distils over, and, after cooling, the residue is mixed with the distillate and used direct (*idem*, E.P., 16100 of 1906; G.P., 188702, 198713; U.S.P., 850827), or 1 part of the acid is heated with 3–5 parts of paraffin at 200–230° or with 5 parts of glycerol for several hours at 200° (*idem*, G.P., 188702), or 1 part of the acid is heated to boiling with 5 parts of aniline for several hours. On cooling or by acidifying the diluted product, the aniline compound is obtained which on boiling with dilute acids furnishes 2-hydroxythionaphthen; this distils over with the steam as white needles (*idem*, G.P., 202351).

By heating the disodium salt of phenylthioglycol-*o*-carboxylic acid (20 kilos.) with 24 kilos. of sodium hydroxide in an oven at 150–200° for one hour (the English and United States patents give 16 parts of sodium hydroxide and the mixture is heated at 250° for one hour), cooling, dissolving in water, and acidifying, 2-hydroxythionaphthen-1-carboxylic acid is precipitated (*idem*, E.P., 16907 of 1906; G.P., 196016; U.S.P., 850827).

Lastly, 10 parts of phenylthioglycol-*o*-carboxylic acid are mixed with 10 parts of glycerol, and 60 parts of sulphuric acid (66° Bé.) are added in a thin stream without cooling. After half an hour water is added and the hydroxythionaphthen is distilled in a current of steam (Badische Anilin- & Soda-Fabrik, G.P., 228914).

Hydroxythionaphthen is also formed by condensing chloroacetic acid with *o*-aminothiophenol to *o*-aminophenylthioglycol-*o*-carboxylic acid, converting this into the cyano-derivative by means of the diazo-reaction, and boiling it with dilute sodium hydroxide to form 2-aminothionaphthen-1-carboxylic acid, which is converted into 2-hydroxythionaphthen by boiling with dilute acid (Kalle & Co., E.P., 11173 of 1906; F.P., 366611; G.P., 184496), or the cyano-derivative is converted direct into 2-hydroxythionaphthen by treatment with sulphuric acid (*idem*, G.P., 190291) or sodium hydroxide solution (*idem*, G.P., 190674).

Alkali salts and esters of methylthiosalicylic acid (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 593 of 1907; F.P., 383744; G.P., 193800, 197520; U.S.P., 889010) can also be converted into 2-hydroxythionaphthen (*idem*, E.P., 1592 of 1907; F.P., 384343; G.P., 200200, 200428, 200593; U.S.P., 894004).

Another method of preparation consists in treating thiosalicylic acid with acetylene dichloride (dichloroethylene), $CHCl{:}CHCl$, whereby acetylenebisthiosalicylic acid,

$$CO_2H{\cdot}C_6H_4{\cdot}S{\cdot}CH{:}CH{\cdot}S{\cdot}C_6H_4{\cdot}CO_2H,$$

is produced, mixing 20 parts of this with 10 parts of potassium hydroxide and 10 parts of sodium hydroxide, and heating the mixture for half an hour at 220–230°. The product is dissolved in water, acidified, and the 2-hydroxythionaphthen driven over with steam (Badische Anilin- & Soda-Fabrik, E.P., 26053 of 1907; F.P., 385044; G.P., 221465; U.S.P., 943560, 943561).

When condensed with trichloroethylene, thiosalicylic acid furnishes ω-dichlorovinylthiosalicylic acid,

$$CO_2H{\cdot}C_6H_4{\cdot}S{\cdot}CH{:}CCl_2,$$

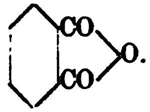
which, on fusion with sodium and potassium hydroxides, gives 2-hydroxythionaphthen or its carboxylic acid (*idem*, E.P., 90 of 1908; F.P., 385044; G.P., 210644).

2-Hydroxythionaphthen-1-carboxylic acid melts at 213° and is sparingly soluble in cold water, benzene, or light petroleum, but dissolves more readily in ethyl acetate, alcohol, or acetone.

2-Hydroxythionaphthen melts at 71° and resembles α-naphthol in its properties.

The compounds are used for making Thioindigo red B, Ciba grey G, Ciba violet B, Helindone brown G, Thioindigo scarlet R and G, Ciba scarlet G, Helindone pink BN, Ciba orange G, etc.

PHTHALIC ANHYDRIDE,



The modern process of preparing phthalic anhydride consists in oxidising naphthalene in the presence of mercuric salts with sulphuric acid, the sulphur dioxide which is evolved being returned to the sulphuric acid plant; the oxidation is thus indirectly brought about by atmospheric oxygen.

$$C_{10}H_8 + 9SO_3 = C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}O + 9SO_2 + 2CO_2 + 2H_2O$$

(Badische Anilin- & Soda-Fabrik, E.P., 18221 of 1896; F.P., 259766; G.P., 91202; U.S.P., 644331).

A kinetic study of the oxidation process has been made by Bredig and Brown (*Zeitsch. physikal. Chem.*, 1903, **46**, 502).

The following is a description of the process. (Compare H. Levinstein, *J. Soc. Dyers*, 1901, **17**, 139, and the article on "Phthalic Acid" in Thorpe's "Dictionary of Applied Chemistry," 1913, IV., 250.)

In a vertical cylinder fitted with a mechanical stirrer, 350 kilos. of naphthalene are dissolved in 3,675 kilos. of sulphuric acid (66° Bé.) and 1,050 kilos. of fuming sulphuric acid (containing 23 per cent. of sulphur trioxide) by stirring for three hours.

The solution (*A*) so prepared is stored in a reservoir until required.

The oxidation vessel consists of an iron pan, built round with bricks and carefully heated by means of gas jets. The pan possesses a removable lid, has a flat bottom, a diameter of 6 feet, and is 2 feet deep; a wide tube for leading off the vapours is provided, and through the top passes a shaft connected with a two-arm stirrer, worked mechanically, which just scrapes the bottom of the pan; also several iron marbles are allowed to rotate on the pan bottom to attract charred matter, and a pressure gauge is inserted on the lid.

The phthalic anhydride sublimes simultaneously with quantities of sulphuric acid which distils over, and these vapours are conducted through a short pipe, 8 inches in diameter, into the condenser, which consists of three concentric lead cylinders fixed one within the other at a distance of about a foot; two of these communicate with one another through the bottom and open into the third, which is surrounded by an outer condenser, through which water is circulated. The third of these cylinders is again connected with a reservoir into which the condensed sulphuric acid overflows. On the lid of the closed condensers is a vacuum arrangement which conducts off the sulphur dioxide as soon as formed, to an absorption apparatus.

At the beginning of the operation the oxidation pan, containing 120 kilos. of sulphuric acid (100 per cent.) and 4 kilos. of mercury, is heated for one and a half hours very gently until all the sulphuric acid distils over, the stirring apparatus being worked during this operation. The prepared solution (*A*) is now admitted into the pan from a storage reservoir above, in portions of 22 litres, and the gas-heating is so regulated that each 22 litres distils over in about thirteen to seventeen minutes.* The end of each operation is observed by the increased noise of the rotating marbles on the bottom of the pan, and a further measured lot of 22 litres is then run in.

The process is continued until the pan contains so much charred matter that it is advisable to clean it. The process of the anhydride formation is controlled by gas analysis, the amount of carbon dioxide evolved being determined from time to time.

When the carbon dioxide content reaches 0·6–0·8 per cent. the addition of naphthalene solution (*A*) is discontinued, and in this emergency three times the volume of sulphuric acid (66° Bé.) is admitted and distilled away, after which the vessel is again ready for two or three days' continuous working. Should the carbon dioxide gas content reach 1 per cent., the work is interrupted for a complete cleaning of the vessel; the pan is heated until perfectly dry, the lid opened, and charred matter chipped from the interior.

To separate the sulphuric acid and phthalic anhydride, which together collect in the condenser, the clear sulphuric acid is first decanted, and then the crude phthalic anhydride is further separated centrifugally and washed free from acid. The product is dried and purified by resublimation in a pan mechanically stirred and heated over a coke fire. A large cylindrical vessel is employed as condenser. The cost of this process, as worked in Germany, is about one mark per kilo. of phthalic anhydride.

The following modification of this process is stated to give an

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* The temperature should be 290–295°.

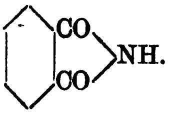
improved yield. Ten lb. of mercury are stirred with 100 lb. of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide) and the temperature is raised to 200°, being kept at that point for an hour. To this is added a solution of 30 lb. of naphthalene in 100 lb. of fuming sulphuric acid of the same strength and the mixture is heated in a retort to 250°, and kept at this point until about half the volume of the mixture has distilled over. During this operation it is essential that the mass is well stirred. It is then cooled to 200° and 100 lb. of fuming sulphuric acid are added; the temperature is raised to about 250°, and after half the volume has distilled over, 150 lb. of fuming sulphuric acid are added and the temperature is raised to about 300°. The distillate is filtered, the residue treated with sodium hydroxide solution, and the filtrate from this is neutralised and evaporated to dryness. The product is purified by sublimation (Ellis-Foster Co., U.S.P., 1261022).

Some other processes have also been patented; thus, naphthols and other naphthalene derivatives are heated in the presence of a very slight excess of alkali, with metallic oxides or peroxides, such as copper and iron oxides or barium, lead or manganese peroxides, to 240–260° for eight hours in an atmosphere of oxygen under pressure (Basle Chemical Works, E.P., 15527 of 1901; F.P., 313187; G.P., 136410, 138790, 139936, 140999; U.S.P., 702171). The use of salts or oxides of the rare metals, such as cerium, lanthanum, neodymium, praseodymium, and ytterbium, has been proposed instead of mercury (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 19178 of 1902; F.P., 328069; G.P., 142144, 149677, 158609; U.S.P., 757136. Compare also Ditz, *Chem. Zeit.*, 1905, **29**, 581). A process for the electrolytic oxidation in sulphuric acid solution in the presence of cerium sulphate has also been described (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 19178 of 1902; F.P., 328069; G.P., 152063; U.S.P., 729502, 757136). The catalytic oxidation of naphthalene vapour by air in the presence of vanadium pentoxide or molybdenum trioxide has been proposed by The Selden Co. and Gibbs (E.P., 119518 [1917]; U.S.P., 1285117).

Phthalic anhydride melts at 128° and boils at 284°. It is very sparingly soluble in cold water, more readily so in hot, being gradually converted into phthalic acid. It is readily soluble in alcohol.

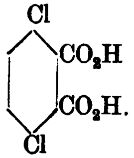
It is used for making Fluorescein, Eosines, Rhodamines, Violamines, Phloxine, Erythrosine, Rose Bengal, Fast acid red A, Fast acid violets, Gallein, Quinoline yellow, and Indigo.

Phthalimide,



See under Anthranilic acid, p. 147.

3 : 6-Dichlorophthalic Acid,



This was formerly prepared by oxidising dichloronaphthalene tetrachloride with nitric acid (Faust, *Annalen*, 1871, **160**, 64; Castélaz, E.P., 447 of 1879), but probably the best method is to chlorinate phthalic anhydride dissolved in fuming sulphuric acid in the presence of iodine (Juvalta, G.P., 50177; see under Tetrachlorophthalic acid, p. 167); the reaction proceeds as follows:

$$C_8H_4O_3 + 4Cl + 2SO_3 = C_8H_2O_3Cl_2 + 2SO_3HCl.$$

In addition to the 3 : 6-dichloro-acid, which is formed to the extent of about 50 per cent., about 30–35 per cent. of the 3 : 4-dichloro-acid and about 15–20 per cent. of the 4 : 5-dichloro-acid are formed.

Villiger (*Ber.*, 1909, **42**, 3529) gives the following account of the preparation.

To a solution of 600 grams of phthalic anhydride in 3·24 kilos. of fuming sulphuric acid (containing 23 per cent. of sulphur trioxide) 2 grams of iodine are added, the solution is thoroughly well stirred, and a slow stream of chlorine introduced, the temperature rising from 40° to 60°. The temperature and the stream of chlorine must be so regulated that only traces of free chlorine or sulphur trioxide are evolved. The better the agitation the quicker is the absorption of chlorine. The operation is finished when the weight of the solution has increased by 580 grams, the introduction of the chlorine taking about forty hours. The whole is warmed until the chlorine dissolved in the liquid has disappeared and the greater part of the chlorosulphonic acid is distilled off up to 250°. The residue, on cooling, solidifies to a mass of crystals. It is mixed with about 4 kilos. of ice, care being taken to avoid undue rise of temperature, and the anhydrides of the dichlorophthalic acids are filtered off. For manufacturing purposes it seems probable that these may be used directly.

The separation of these acids was effected by Villiger as follows: The paste is treated with about 4 litres of hot water, whereby the anhydrides are hydrolysed, the excess of sulphuric acid is removed by adding barium chloride, the barium sulphate filtered off, and the filtrate exactly neutralised with sodium carbonate. To the boiling solution is added a concentrated solution of 300 grams of zinc chloride, the mixture kept hot for an hour, and the precipitate filtered off. The filtrate is heated to boiling and a solution of calcium chloride added until a filtered sample, on boiling with more calcium chloride, gives no further precipitate. This precipitate is also filtered off. Pure 3 : 6-dichlorophthalic anhydride is obtained from it by decomposition with hydrochloric acid and extraction with ether.

The zinc precipitate containing the mixture of the 3 : 4- and 4 : 5-dichloro-acids is treated with 1·2 litres of hot 25 per cent. sulphuric acid and, on cooling, much dichloro-acid separates out. Sometimes this consists of almost pure 3 : 4-acid, but is usually a mixture of the two. On extraction with ether, evaporation, and distillation of the mixture of anhydrides, the 4 : 5-dichlorophthalic anhydride is obtained pure from the distillate by crystallisation from the smallest possible quantity of toluene. The 3 : 4-anhydride, which remains in the toluene mother liquor, is obtained by hydrolysing the residue after evaporating off the toluene and crystallising the acid repeatedly from dilute hydrochloric acid.

Pratt and Perkins (*J. Amer. Chem. Soc.*, 1918, **40**, 216) passed a slow stream of chlorine through a solution of 1,500 grams of phthalic anhydride in 1,500 grams of fuming sulphuric acid (containing 50 per cent. of sulphur trioxide) at 60–70° for about forty hours. The separation was effected by Villiger's method, the calcium precipitate weighing 974 grams and the zinc salt 1,746 grams. The yield of pure anhydrides is stated to be very poor in comparison with these figures, especially in the case of the 3 : 4- and 4 : 5-anhydrides, which are difficult to separate.

Graebe (*Ber.*, 1900, **33**, 2019) states that the technical product always contains some trichloro-acid and gives a method for purifying it for scientific work.

The melting and boiling points of these anhydrides are given below:

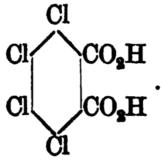
	M.p.	B.p.
3 : 6-Dichlorophthalic anhydride	190—191°	339°
3 : 4- „ „	120—121	329
4 : 5- „ „	185—187	313

3 : 6-Dichlorophthalic acid is easily converted into its anhydride by heating it below the melting point.

Both the neutral and acid sodium, potassium, and ammonium salts are readily soluble in water, the calcium and barium salts are sparingly soluble, whilst the zinc salt, unlike those of the isomeric acids, is readily soluble.

3 : 6-Dichlorophthalic acid is used for making New pink (Phloxine P) and Rose Bengale.

TETRACHLOROPHTHALIC ACID,



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The earlier method of preparing this was to pass a stream of chlorine into a mixture of phthalic anhydride (1 part) and antimony pentachloride (6 parts) heated to 200°, the antimony pentachloride being first distilled off and then the tetrachlorophthalic anhydride (Society of Chemical Industry in Basle, G.P., 32564; Gnehm, U.S.P., 322368, *Annalen*, 1887, 238, 320), but an improved method is due to Juvalta (G.P., 50177), according to which 10 kilos. of phthalic anhydride, 30 kilos. of fuming sulphuric acid (containing 50–60 per cent. of sulphur trioxide), and 0·5 kilo. of iodine are mixed together in a cast iron pan and chlorine is led in at 50–60°. The mass becomes thick owing to the separation of the chlorinated product, and the temperature is gradually raised to 200°. When, at this temperature, all the iodine has disappeared as iodine chloride, the operation is finished. The reaction is represented by the equation:

$$C_8H_4O_3 + 8Cl + 4SO_3 = C_8Cl_4O_3 + 4SO_3HCl.$$

At the end of the operation the bulk of the chlorosulphonic acid is distilled off and the residue is mixed with ice sufficient to bring the temperature below 50°. The tetrachlorophthalie anhydride is filtered off, washed, and dried.

Pratt and Perkins (*J. Amer. Chem. Soc.*, 1918, **40**, 204) heated a mixture of 500 grams of phthalic anhydride, 2,000 grams of fuming sulphuric acid (containing 50 per cent. of sulphur trioxide) and 10 grams of iodine to 70° and passed a stream of chlorine through it for about forty hours. During the first few hours the temperature was increased to about 100° and maintained at that point until the last few hours, when it was raised to 180°. The mixture was cooled, and slowly treated with water, the product filtered off and digested with water at 100°.

Tetrachlorophthalic anhydride is insoluble in cold water and melts at 252°. On boiling with sodium carbonate solution and adding mineral acid, the corresponding acid is obtained, which crystallises with $\frac{1}{2}H_2O$, and when heated to 109° it is completely converted into the anhydride (Delbridge, *Amer. Chem. J.*, 1909, **41**, 393).

It is used for making Phloxine and Rose Bengale.

DIHYDROXYTARTARIC ACID,* $CO_2H\cdot C(OH)_2\cdot C(OH)_2\cdot CO_2H$.

27·6 Kilos. of finely powdered dry tartaric acid are added to a mixture of 16·4 kilos. of fuming sulphuric acid (containing 30 per cent. of sulphur trioxide), 13·4 kilos. of sulphuric acid (66° Bé.), and 33·4 kilos. of nitric acid (40° Bé.) contained in an enamelled iron pan which can be cooled and is fitted with a stirrer. The temperature is kept at about 20° and the mixture stirred for three hours. One hundred and fifty kilos. of ice are now added, and stirring is continued. Nitrous fumes are evolved, and at the end of about forty-eight hours, the temperature having been kept at about 20°, the decomposition is complete. The mixture is neutralised cold with 86 kilos.of sodium carbonate, and the almost insoluble sodium salt filtered off, washed, and dried. The yield is about 75 per cent. of the theoretical (*Rev. prod. chim.*, 1917, **20**, 22).

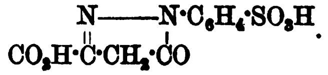
The acid is very unstable. The sodium salt crystallises with $2H_2O$ and is almost insoluble in water.

Dihydroxytartaric acid is used for making Tartrazine (Buffalo yellow).

PYRAZOLONES.

1-*p*-SULPHOPHENYL-5-PYRAZOLONE-3-CARBOXYLIC ACID

(TARTRAZINOGENSULPHONIC ACID),



$$\begin{array}{l} \qquad\quad N\text{———}N\cdot C_6H_4\cdot SO_3H \\ CO_2H\cdot\overset{\|}{C}\cdot CH_2\cdot\overset{|}{C}O \end{array}.$$

(1) Nineteen kilos. of phenylhydrazine-*p*-sulphonic acid (p. 49) are suspended in 100 litres of water, 18·8 kilos. of ethyl oxalate

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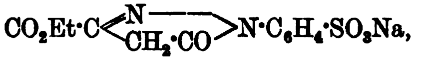
* Although this acid does not, of course, belong to the benzene series it is conveniently included here.

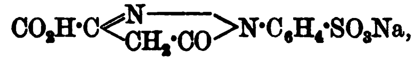
and 15 kilos. of crystallised sodium acetate are added, and the mixture is stirred at 50° until the condensation is complete. The product is not isolated but used direct (Ziegler, E.P., 5693 of 1893).

(2) Ninety-five grams of phenylhydrazine-*p*-sulphonic acid are stirred with a solution of 75 grams of sodium acetate in 500 c.c. of water, 94 grams of ethyl oxalacetate are added, and the mixture is stirred and heated at 50° until a clear solution is obtained. After one to two days it sets to a crystalline mass. If the mixture is heated to boiling for a short time, instead of to 50°, the solution crystallises at once on cooling. The material is collected and a further quantity of the ethyl ester of the pyrazolone separates on keeping the filtrate. This is filtered off, the filtrate rendered alkaline with sodium hydroxide, evaporated on the water-bath, and acidified, when a small amount of the acid sodium salt of the pyrazolone is obtained.

The main quantity of the ester is mixed with 10 parts of water and heated on the water-bath with rather more than 2 mols. of sodium hydroxide to 1 mol. of the salt,



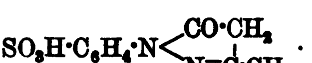
$$CO_2Et\cdot C{<}\genfrac{}{}{0pt}{}{N\text{———}}{CH_2\cdot CO}{>}N\cdot C_6H_4\cdot SO_3Na,$$

for half an hour. The hot, clear solution is acidified with dilute hydrochloric acid and, on cooling, small crystals of the acid sodium salt,  $CO_2H\cdot C{<}\genfrac{}{}{0pt}{}{N\text{———}}{CH_2\cdot CO}{>}N\cdot C_6H_4\cdot SO_3Na$, separate (Anschütz, *Annalen*, 1896, 294, 234).

The acid sodium salt crystallises with $2H_2O$ and is very sparingly soluble in cold water.

It is used for making Flavazine S (Hydrazine yellow SO).

1-*p*-SULPHOPHENYL-3-METHYL-5-PYRAZOLONE,



$$SO_3H\cdot C_6H_4\cdot N{<}\genfrac{}{}{0pt}{}{CO\cdot CH_2}{N{=}\overset{|}{C}\cdot CH_3}\;.$$

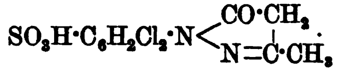
This was obtained by Möllenhoff (*Ber.*, 1892, 25, 1941) by heating phenylmethylpyrazolone with 4 parts of fuming sulphuric acid (containing 30 per cent. of sulphur trioxide) on the water-bath; on pouring into water, the acid crystallises out.

It is manufactured by warming phenylhydrazine-*p*-sulphonic acid with ethyl acetoacetate in 50 per cent. acetic acid for three hours.

The acid is sparingly soluble in cold water and crystallises with 1H_2O.

It is used for making Fast light yellows G, 2G, and 3G (Flavazine L).

2′ : 5′-Dichloro-4′-sulpho-1-phenyl-3-methyl-5-pyrazolone,



$$SO_3H\cdot C_6H_2Cl_2\cdot N\begin{cases}CO\cdot CH_2\\ N=\overset{|}{C}\cdot CH_3\end{cases}.$$

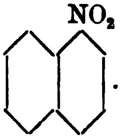
This is prepared by condensing ethyl acetoacetate with 2 : 5-dichlorophenylhydrazine-4-sulphonic acid (obtained from 2 : 5-dichloroaniline-4-sulphonic acid ; see preparation of phenylhydrazine-*p*-sulphonic acid, p. 49) in an analogous manner to 1-*p*-sulphophenyl-5-pyrazolone-3-carboxylic acid (p. 168) (Chemische Fabrik vorm. Sandoz, E.P., 3373 of 1908 ; F.P., 387245 ; G.P., 222405 ; U.S.P., 901675).

It is used for making Xylene yellow 3G.

Naphthalene Series.*

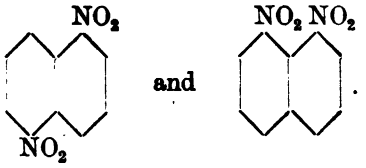
Nitro-compounds.

α-Nitronaphthalene,



See under α-Naphthylamine, p. 181.

1 : 5- *and* 1 : 8-Dinitronaphthalenes,



These two dinitro-derivatives are produced by the nitration of α-nitronaphthalene, the proportion of the 1 : 5- to the 1 : 8-derivative being about 1 : 2.

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* For the chemistry of the naphthalene series the excellent article by Wynne ("Naphthalene") in Thorpe's "Dictionary of Applied Chemistry" should be consulted.

One hundred kilos. of naphthalene are mixed with 310 litres of crude nitric acid and the whole allowed to remain for a day; 160 litres of sulphuric acid are then added and the mixture is kept at 90–100° for a day. The product is washed with water and dried. It is extracted with carbon disulphide to remove mononitronaphthalene and then with acetone to remove 1 : 8-dinitronaphthalene, the latter extraction being prolonged until the residue of 1 : 5-dinitronaphthalene melts at 210° (Ristenpart, "Organische Farbstoffe," 1911, p. 11).

One hundred grams of nitronaphthalene are dissolved in 600 grams of sulphuric acid (66° Bé.) and treated at 0° with a mixture of 52 grams of nitric acid (D 1·4) and 260 grams of sulphuric acid. The mixture is then warmed to 80–90° until the dinitro-compounds are dissolved. On cooling to 20°, almost the whole of the 1 : 5-dinitronaphthalene separates in needles which are filtered off through asbestos. The 1 : 8-compound is precipitated from the filtrate by adding water and purified by recrystallisation from pyridine or benzene (Friedländer, *Ber.*, 1899, **32**, 3531; Kalle & Co., G.P., 117368). This is a more convenient process than that given by Gassmann (*Ber.*, 1896, **29**, 1243, 1521).

Eckstein (*Ber.*, 1902, **35**, 3403) found that 1 : 5-dinitronaphthalene is not attacked by fuming sulphuric acid below 140°, whilst the 1 : 8-derivative is converted into a sulphonic acid. 1 : 5-Dinitronaphthalene, containing a little of the 1 : 8-derivative, can thus be purified by heating it on the oil-bath with fuming sulphuric acid (containing 15–25 per cent. of sulphur trioxide). On pouring into water, the sulphonic acid remains in solution. On the other hand, the statement has been made (Farbwerke vorm. Meister, Lucius, & Brüning, G.P., 117268) that 1 : 5-dinitronaphthalene can be sulphonated to the 3-sulphonic acid.

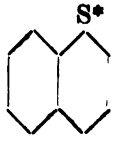
If the technical mixture (200 kilos. of a 60 per cent. paste) is warmed for five to six hours at 80–90° with 740 kilos. of sodium hydrogen sulphite (40 per cent.) and 140 kilos. of ammonia (25 per cent.), the 1 : 5-compound is not attacked and may be filtered off, whilst the 1 : 8-compound is converted into 1-naphthylamine-4 : 7-disulphonic acid (Farbwerke vorm. Meister, Lucius, & Brüning, G.P., 221383).

1 : 5-Dinitronaphthalene melts at 216°. The crude mixture with the 1 : 8-compound is used for making Alizarin black, etc., and the 1 : 5-compound itself for making Melanogen blue.

1 : 8-Dinitronaphthalene melts at 170° and is used for making Fast black B and Cryogen brown A.

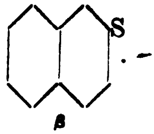
NAPHTHALENESULPHONIC ACIDS.

NAPHTHALENEMONOSULPHONIC ACIDS,



α

and



β

As is well known, the action of sulphuric acid on naphthalene at a low temperature gives naphthalene-α-sulphonic acid, whilst at a high temperature the β-acid is the main product. Thus Merz and Weith (*Ber.*, 1870, 3, 195) state that a mixture of naphthalene and sulphuric acid in the proportion of 10 : 9 gave a product containing 80 per cent. of α-acid and 20 per cent. of β-acid when heated for three hours at 100°, but only 25 per cent. of α-acid with 75 per cent. of β-acid when heated for a further four hours at 170°, 15 per cent. of the naphthalene employed being recovered in the first case and 25 per cent. in the second. Also, that a mixture in the proportion 5 : 4 heated for eight hours at 160° gave 80 per cent. of β-acid, 30 per cent. of the naphthalene employed being recovered.

When finely powdered naphthalene is sieved into 1½–2 times its weight of sulphuric acid at 40°, and the mixture stirred for many hours until everything has dissolved, the α-acid is said to be the sole product, and the same result is obtained, but more rapidly, when sulphonation is effected by fuming sulphuric acid in the cold (Chemische Fabrik Grünau, Landshoff & Meyer, G.P., 50411).

Euwes (*Rec. trav. chim.*, 1909, 28, 298) made a quantitative study of the interaction of equimolecular quantities of naphthalene and 100 per cent. sulphuric acid at various temperatures for eight hours, and the following table shows the results of these experiments :

	Naphthalene recovered.	Percentage in product of		
Temperature.	Per cent.	α-acid.	β-acid.	Sulphone.
80°	27·0	96·4	3·6	—
100°	20·0	83·2	16·8	—
129°	10·0	44·4	55·6	1·0
138·5°	8·6	28·4	71·6	(?)
150°	6·4	18·3	81·7	3·2

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* In the naphthalene series, it is convenient to use this sign to indicate SO_3H.

Experiments in which the duration of heating was varied show that the primary product of sulphonation is the α-acid, which is gradually transformed into the β-isomeride. Thus after thirty-five minutes at 129° the product contains 79·1 per cent. of the α-acid, whilst after six hours the proportion is reduced to 45·1 per cent. At 143° and 158°, however, equilibrium is attained. The transformation of one acid into the other is due to the hydrolysis of the two acids into naphthalene and sulphuric acid and subsequent resulphonation, the α-acid being more stable at low and the β-acid at high temperatures. Addition of sulphur trioxide largely increases the amount of sulphone formed. Lead and mercuric sulphates have practically no effect on the reaction.

Preparation of Naphthalene-α-sulphonic Acid.—One hundred kilos. of finely ground naphthalene are gradually added to 175 kilos. of sulphuric acid contained in a sulphonating pan, the temperature being kept at 50°. Towards the end of the reaction the temperature may be raised to 80° (Chemische Fabrik Grünau, Landshoff and Meyer, G. P., 50411.) When the naphthalene is practically all sulphonated, the mixture is blown into 2,500 litres of water and the α-acid isolated as sodium salt as described for the β-acid (below).

The acid melts at 85–90° and is sparingly soluble in slightly dilute sulphuric acid. The sodium salt can be salted out of solution, but is more readily soluble than the sodium salt of the β-acid. The calcium salt crystallises with $2H_2O$, and dissolves in 16·5 parts of water or 19·5 parts of 85 per cent. alcohol at 10–11°.

It is used for making α-naphthol and various naphthol- and naphthylamine-sulphonic acids.

Preparation of Naphthalene-β-sulphonic Acid.—The sulphonation pan must be capable of being heated to 200° and must be furnished with a good agitator. Arrangement must also be made whereby a little naphthalene and water may distil over. (The plant is shown in Fig. 23.)

One hundred kilos. of naphthalene are melted, heated to 160°, and 100 kilos. of sulphuric acid (66° Bé.) gradually added, the temperature being kept constant. The mixture is maintained at this temperature for a further three hours, and is then heated at 170° for an hour and subsequently at 180° for the same time. Three or four kilos. of naphthalene distil over. The reaction is over when a sample dissolves completely in water.

The product is now blown into 2,500 litres of water and converted into sodium salt. This may be done by neutralising with

50–60 kilos. of lime, filtering, and converting the calcium salt into sodium salt by treating the filtrate with about 40 kilos. of sodium carbonate, filtering, and evaporating to crystallising point.* The sodium salt of the β-acid separates out, whilst the sodium salt of the α-acid remains in the mother liquor.

It is simpler, however, to salt out the acid, after being poured into 2,500 litres of water, by adding common salt or sodium sulphate, or by neutralising with about 40 kilos of sodium carbonate. The sodium salt obtained in this way is filtered in a filter press and dried, preferably in a vacuum drier. The yield is about 160–165 kilos. (Grandmougin, *Rev. prod. chim.*, 1917, **20**, 197).

If, in the subsequent melting operation, the sodium β-naphthoxide is allowed to settle on the surface of the mixture of sodium hydroxide and sodium sulphite and then separated, this mixture may be used to form the sodium salt of the β-acid (Levinstein, E.P., 2300 of 1883; see also Uhlmann, E.P., 24826 of 1906; F.P., 371089; G.P., 229537, who uses crude sodium sulphite).

By adding ferrous sulphate to the sulphonation mixture, the β-salt is precipitated and is converted into the sodium salt by means of sodium carbonate. The α-acid in the mother liquor is recovered by treating it with milk of lime, filtering, making the sodium salt, and evaporating the solution (S. B. Boulton, Haywood, H. E. Boulton and Fergusson, E.P., 4459 of 1894).

It has also been proposed to extract the β-acid from the sulphonation mixture by means of toluene (Dennis, E.P., 109709 [1916]; U.S.P., 1228414). (See also under Phenol.)

Witt (*Ber.*, 1915, **48**, 743), who has made a special study of naphthalene-β-sulphonic acid, heats 250 grams of naphthalene to 160° and adds 400 grams of sulphuric acid (93·7 per cent), the temperature being kept constant; the operation requires about fifteen minutes for the above amounts. After heating for a further five minutes, the sulphonation mixture is allowed to remain for a short time, and is then poured into 300 c.c. of water. At this concentration, the β-acid is salted out by the α-acid present, and, on cooling, nearly all the β-acid separates as trihydrate. About 1 per cent. of sulphone is present. The proportion of the two acids formed is 85 of the β-acid to 15 of the α-acid. The β-acid may be purified by dissolving 600 grams in 300 c.c. of water at 70° and allowing to cool after the addition of 100 c.c. of hydrochloric acid (D 1·19).

The sodium salt crystallises with $1H_2O$, and dissolves in 16·5

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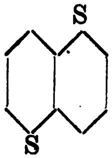
* For the many proposed variations of this process, see under Phenol, and also Southcombe and Downie, E.P., 120405 [1917].

parts of water and in 15·4 parts of *N*- or 41 parts of 5*N*-hydrochloric acid at 23·9° (Fischer, *Ber.*, 1906, 39, 4144). The calcium salt dissolves in 76 parts of water or 437 parts of 85 per cent. alcohol at 10–11°.

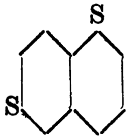
It is used for making β-naphthol and for various other sulphonic acids.

NAPHTHALENE-DI- *and* -TRI-SULPHONIC ACIDS.

The following are the technically important disulphonic acids of naphthalene (S = SO_3H) :—



1 : 5.



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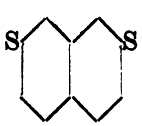

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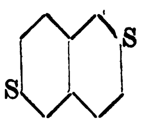


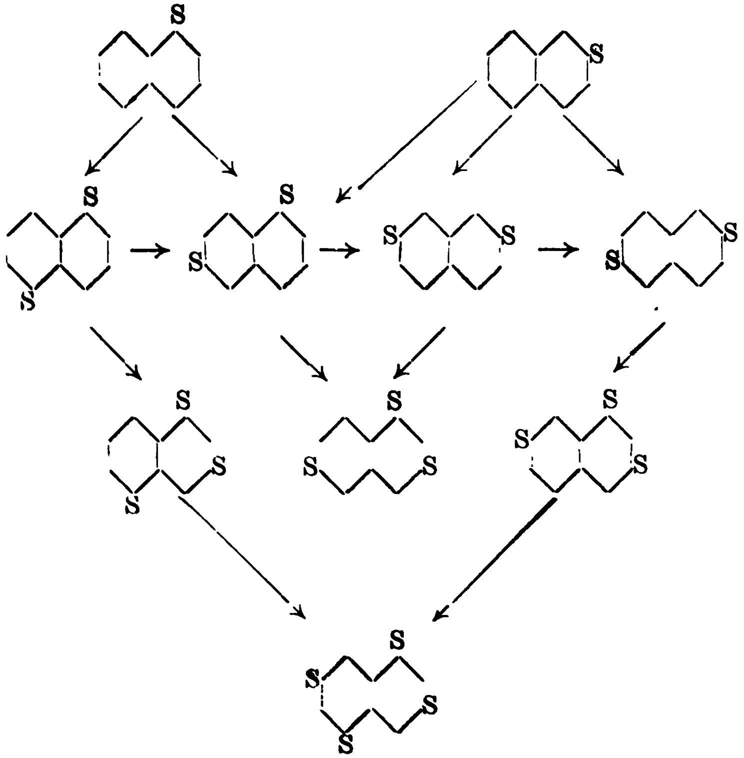
2 : 6.

The 1 : 5- and 1 : 6-acids are obtained by sulphonating naphthalene-α-sulphonic acid, and the 2 : 7- and 2 : 6-acids from naphthalene-β-sulphonic acid.

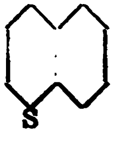
On sulphonating the α-acid at a low temperature, the tendency is for the new sulphonic group to enter the furthest α-position (that is, 5), and just as naphthalene-α-sulphonic acid on further heating with sulphuric acid is converted into the β-acid (through hydrolysis and resulphonation), so the 1 : 5-disulphonic acid under analogous conditions is converted into the 1 : 6-acid. When the β-acid is sulphonated at a low temperature, some of the 1 : 6-disulphonic acid is formed, but at a higher temperature mainly the 2 : 7- and 2 : 6-disulphonic acids. The 1 : 6-acid thus passes into the 2 : 7-acid on further heating, and the 2 : 7-acid into the 2 : 6. It is practically impossible to arrange the conditions so that one acid is formed to the exclusion of others, accordingly from naphthalene-α-sulphonic acid (or naphthalene) a mixture of the 1 : 5- and 1 : 6-acids is produced at a low temperature, and from the β-acid (or naphthalene) a mixture of the 2 : 6- and 2 : 7-acids at a high temperature.

Of the trisulphonic acids, the 1 : 3 : 5- and 1 : 3 : 6-acids are the most important. The former is produced by sulphonating the 1 : 5-disulphonic acid, and the latter by sulphonating the 1 : 6- or the 2 : 7-acid. The 1 : 3 : 6-acid is usually prepared either from naphthalene direct or from naphthalene-β-sulphonic acid, and consequently is accompanied by some of the 1 : 3 : 5-acid.

The following scheme illustrates the above relationships :—



NAPHTHALENE-1 : 5-DISULPHONIC ACID,

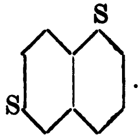


Preparation from Naphthalene.—One hundred kilos. of fuming sulphuric acid (containing 23 per cent. of sulphur trioxide) are added gradually to 20 kilos. of naphthalene, the temperature being kept below 60° and the mixture stirred until all the naphthalene has dissolved (Aktiengesellschaft für Anilinfabrikation, E.P., 4625 of 1888 ; F.P., 189712 ; G.P., 45776), or 100 kilos. of naphthalene are melted within one to two hours at about 80°, and 280 kilos. of fuming sulphuric acid are added slowly during four to five hours, during which time the heating is discontinued (Paul, *Zeitsch. angew. Chem.*, 1896, **9**, 559). If four times the weight of fuming sulphuric acid (containing 30 per cent. of sulphur trioxide) is used and the product poured into 3–4 parts of water, a quantitative separation of the 1 : 5-acid is obtained (Ewer and Pick, G.P. Anm. E., 2619 of 1889). This acid may be also separated from the 1 : 6-acid by salting out the sulphonation product.

Preparation from Naphthalene-α-sulphonic Acid.—One part of sodium naphthalene-α-sulphonate is added to 2 parts of fuming sulphuric acid at 20° and the mixture heated for an hour at 60–70°. The mass is poured into 10 parts of water and an equal volume of hot salt solution added. On cooling, the sodium salt of the 1 : 5-acid separates out; this is filtered off and recrystallised from 4 parts of water.

The sodium salt crystallises with $2H_2O$, and dissolves in 8·78 parts of water at 16·5° (or in 7·99 parts at 19°). On nitration, the acid gives 1-nitronaphthalene-4 : 8-disulphonic acid with a little 2-nitronaphthalene-4 : 8-disulphonic acid.

NAPHTHALENE-1 : 6-DISULPHONIC ACID,



Preparation from Naphthalene, or Naphthalene-α-sulphonic Acid.—The preparation is described under naphthalene-1 : 5-disulphonic acid. The acid is also obtained when naphthalene is heated with five times its weight of sulphuric acid (100 per cent.) at 90–100°, or with sulphuric acid at 90° and subsequently with fuming sulphuric acid at 110–120° (G.P. Anm. B., 9514 of 1889; Bernthsen, *Ber.*, 1889, **22**, 3328; Schultz., *Ber.*, 1900, **23**, 77).

Preparation from Naphthalene-β-sulphonic Acid.—Sodium naphthalene-β-sulphonate is heated gently with 2 parts of fuming sulphuric acid (containing 25 per cent. of sulphur trioxide), finally at the temperature of the water-bath, or it is heated with 5 parts of ordinary sulphuric acid for some hours at 110°. The product is converted into the sodium salt, and the solution on concentration deposits needles (Ewer and Pick, G.P., 45229).

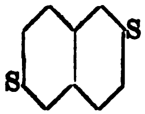
Alternatively, 200 kilos. of the product of sulphonation of naphthalene to the β-acid (corresponding with 100 kilos. of naphthalene) are heated with 400 kilos. of sulphuric acid (66° Bé.)

for twenty to twenty-four hours to 95–100° (Paul, *Zeitsch. angew. Chem.*, 1896, 9, 561).

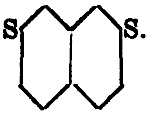
The sodium salt crystallises with $7H_2O$ and dissolves in 3·34 parts of water at 16·5°.

On nitration, the acid gives 1-nitronaphthalene-3 : 8-disulphonic acid with a little 2-nitronaphthalene-4 : 7-disulphonic acid.

NAPHTHALENE-2 : 6- *and* 2 : 7-DISULPHONIC ACIDS,



and



Preparation from Naphthalene.—Naphthalene is heated with five times its weight of sulphuric acid at 160° for five hours, the product poured into water, and converted into the calcium salt. The separation of the isomeric disulphonic acids can be based on the very sparing solubility in water of the calcium salt of the 2 : 6-acid after it has been dehydrated at 200–230° (Ebert and Merz, *Ber.*, 1876, 9, 592 ; Freund, E.P., 1069 of 1883 ; F.P., 153847 ; G.P., 27346). Alternatively, advantage may be taken of the difference in solubility of the calcium salts of the 2 : 6-, 2 : 7-, and 1 : 6-acids in concentrated salt solution, as the salt of the 2 : 6-acid is practically insoluble in either hot or cold salt solution ; the salt of the 2 : 7-acid is moderately soluble in hot but very sparingly so in cold, whilst the salt of the 1 : 6-acid is fairly readily soluble in cold salt solution (Chemische Fabrik Grünau, Landshoff, & Meyer, G.P., 48053).

Thus the sulphonation mixture from 200 kilos. of naphthalene and 1,000 kilos. of sulphuric acid is converted into calcium salts in the usual way and the solution, after filtering off the gypsum, evaporated to about 3 cubic metres ; 900 kilos. of common salt are then stirred in, the whole is boiled, and filtered hot from the calcium salt of the 2 : 6-acid. On cooling to about 15°, the 2 : 7-salt separates, and is filtered and pressed. It is converted into sodium salt in the usual way and the solution evaporated to crystallisation. After filtering off the sodium salt, the filtrate can be evaporated and the sodium chloride which separates can be used for the next batch.

The crude calcium salts may also be evaporated to about 1 cubic metre, filtered hot from gypsum and the salt of the 2 : 6-acid, the filtrate stirred with 200 kilos. of common salt, and allowed to cool. The salt of the 2 : 7-acid is filtered, pressed, and redissolved in 7–10 parts of saturated salt solution, again filtering from undissolved salt of the 2 : 6-acid.

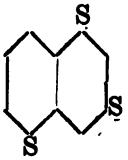
Preparation from Sodium Naphthalene-β-sulphonate.—Two hundred and thirty kilos. of the sodium salt are added to 500 kilos. of sulphuric acid (100 per cent.) or 600 kilos. of ordinary sulphuric acid at 160–170°, and afterwards heated at 180° for six to eight hours. The product is converted into calcium salt, and this solution is concentrated until it contains about 30 per cent. of the salt and then allowed to cool. By this means, the greater part of the calcium salt of the 2 : 6-acid (52 kilos.) is separated. The filtrate is converted into sodium salt and the solution evaporated to dryness. From this the sodium salt of the 2 : 7-acid (200 kilos.) is extracted by 2 parts of warm water, the solution being cooled to 20° before filtration. The residue (80 kilos.) is a mixture of the sodium salts of the 2 : 6- and 2 : 7-acids, which is added to a subsequent batch after liming.

Preparation from Naphthalene-β-sulphonic Acid.—Three hundred kilos. of potassium pyrosulphate are dissolved in 250 kilos. of fused naphthalene-β-sulphonic acid at 160–165°, and 120 kilos. of sulphuric acid (100 per cent.) or 150 kilos. of ordinary sulphuric acid, also heated to 160–170°, added to the solution. The mass is treated with lime and the potassium salts are obtained in the filtrate, which is evaporated until it is about three times the weight of the solid matter. All the salt of the 2 : 6-acid (54–60 kilos.) separates (1 part dissolves in 19 parts of water, whilst 1 part of the salt of the 2 : 7-acid dissolves in 1·4 parts) and the filtrate yields the salt of the 2 : 7-acid (386–390 kilos.).

The sodium salt of the 2 : 6-acid crystallises with $1H_2O$ and dissolves in 8·4 parts of water at 19°; the sodium salt of the 2 : 7-acid crystallises with $6H_2O$ and dissolves in 2·2 parts of water at 18°.

On nitration, the 2 : 6-acid gives 1-nitronaphthalene-3 : 7-disulphonic acid, and the 2 : 7-acid 1-nitronaphthalene-3 : 6-disulphonic acid.

NAPHTHALENE-1 : 3 : 5-TRISULPHONIC ACID,



This is prepared by sulphonating the 1 : 5-disulphonic acid. Erdmann (*Ber.*, 1899, **32**, 3188) added 2 kilos. of sodium naphthalene-1 : 5-disulphonate to 3 kilos. of sulphuric acid (100 per cent.) at a temperature not exceeding 50°, which operation required one hour. In the course of another hour, 2·8 kilos. of fuming sulphuric acid (containing 67 per cent. of sulphur trioxide) were added, care being again taken that the temperature did not rise above 50°. The mass became thinner, and was then heated for 3½ hours at 90°, when the reaction was finished, and 400 grams of ice were added to destroy the excess of sulphur trioxide. The mixture was then neutralised with milk of lime and the calcium salt converted into sodium salt in the usual way, the solution of the latter being evaporated to dryness.

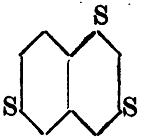
Alternatively, 100 parts of sodium naphthalene-1 : 5-disulphonate are stirred into 300 parts of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide). The temperature rises to about 60–80°, and the mass is then slowly heated to 130°. The disulphonate does not dissolve in the sulphuric acid below 125–130°, but suddenly dissolves at this point, and is then converted into the trisulphonic acid. On diluting a sample with water and saturating with common salt no precipitate of the sodium salt of the disulphonic acid should be obtained. The mixture may be neutralised with slaked lime, and the solution of the sodium salt of the trisulphonic acid may be evaporated to dryness, but for the purpose of making 1-naphthylamine-4 : 6 : 8-trisulphonic acid the sulphonation mixture is directly nitrated (Farbenfabriken vorm. F. Bayer & Co., E.P., 17141C of 1893; F.P., 237872; G.P., 78604, 80741; G.P. Anm. F., 7004, 7006, 7059, K. 11104; U.S.P., 563382).

A variation of the above consists in adding 10 parts of sodium naphthalene-1 : 5-disulphonate to 40 parts of sulphuric acid (100 per cent.) and mixing with it, at 40°, 9 parts of fuming sulphuric acid (containing 70 per cent. of sulphur trioxide), the whole being heated to 80–90° until a sample, diluted with water, gives no precipitate on adding salt. The mixture of naphthalene-1 : 3 : 5-trisulphonic acid is then nitrated direct (Kalle & Co., E.P., 515 of 1894; G.P., 93700, 99164; U.S.P., 563383, 563384).

The acid is very readily soluble in water; the sodium salt crystallises with $4H_2O$ and is also very readily soluble.

-It is used for making 1-naphthylamine-4 : 6 : 8-trisulphonic acid.

NAPHTHALENE-1 : 3 : 6-TRISULPHONIC ACID,



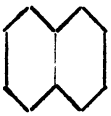
According to Gürke and Rudolph (E.P., 15716 of 1885; F.P., 173007; G.P., 38281), this acid is prepared (1) by adding 1 part of naphthalene gradually to 8 parts of fuming sulphuric acid (containing 24 per cent. of sulphur trioxide) and heating the mixture for some hours at 180°, or (2) by adding 1 part of naphthalene to 6 parts of fuming sulphuric acid (containing 40 per cent, of sulphur trioxide) at a temperature not exceeding 80° and then heating the mixture on the water-bath until the trioxide has disappeared. The 1 : 3 : 5-trisulphonic acid is also produced in this reaction, and is preferably formed at a low temperature, so that the first is the better of these two methods.

A saving in fuming sulphuric acid is effected by starting from sodium naphthalene-β-sulphonate, of which 230 kilos. are added to 430 kilos. of fuming sulphuric acid (containing 40 per cent. of sulphur trioxide) at a temperature not exceeding 60°. The mixture is then warmed slowly to 125° and kept at that temperature for an hour; it is then raised to 160–170° and kept at this point for ten hours. In this case, also, the 1 : 3 : 5-trisulphonic acid is formed, but only a single product is obtained by sulphonating naphthalene-1 : 6- or -2 : 7-disulphonic acids.

The sodium salt crystallises with $5H_2O$ and is very readily soluble in water. It is used for making 1-naphthol-3 : 6-disulphonic acid and 1-naphthylamine-3 : 6 : 8-trisulphonic acid.

NAPHTHYLAMINES AND THEIR SULPHONIC ACIDS.

α–NAPHTHYLAMINE,



The manufacture of this product is described by Witt (*Chem. Ind.*, 1887, **10**, 215) as follows:

Preparation of Nitronaphthalene.—For the nitration a shallow, wide nitrator is used. The stirring arrangement consists of four to six arms set at an angle of 45°. The nitrator is jacketed for water cooling. It is made of cast iron and has a lid of which half is movable, whilst the other half carries a flue; the bottom half of this is steam-jacketed so as to allow any sublimed naphthalene to be melted and run down.

The charge is 250 kilos. of naphthalene, 200 kilos. of nitric acid (40° Bé.), and 200 kilos. of sulphuric acid (66° Bé.) mixed with the nitric acid. Also 600 kilos. of waste acid from a previous operation are mixed with the sulphuric and nitric acids. When the nitrating acid is all in the pan, the sieved naphthalene is added gradually, the temperature being kept at 45–50° until towards the end, when it is raised to 60°. The nitration of the above quantity of naphthalene takes one day. The contents of the pan are run out into a lead-lined tub, and, on cooling, the nitronaphthalene settles to the top as a cake, so that the clear waste acid below can be run off. The nitronaphthalene is freed from adhering acid by boiling with water and granulated by adding cold water with stirring. No β-nitronaphthalene is formed. The yield should be about 95 per cent. of the theoretical.

Triller (G.P., 100417) obtains nitronaphthalene by passing an electric current through a mixture of 1 part of naphthalene and 50 parts of nitric acid (D 1·33) at 80°. This patent was allowed to expire the year after it was taken out.

α-Nitronaphthalene melts at 61° and boils at 304°. One hundred parts of alcohol (87·5 per cent.) dissolve 2·81 parts of nitronaphthalene at 15°. Its density is 1·341 at 4°.

Reduction.—The reduction pan is the same as for aniline, except that no condenser is required: instead of this, a simple, wide tube is fixed. For the reduction, 600 kilos. of air-dried nitronaphthalene, 800 kilos. of iron, and 40 kilos. of hydrochloric acid are used. Iron and acid, together with some water, are mixed and warmed and then the nitronaphthalene is added gradually through the hole provided with a wooden stopper. The addition is so regulated that the pan feels warm on the outside, which corresponds with an inside temperature of about 50°. When all the nitronaphthalene is in, the apparatus is run for six to eight hours longer, the temperature being maintained by blowing steam through the hollow stem of the stirrer. Tests are taken from time to time to see that no nitro-compound is present (by distillation and solution of the distillate in hydrochloric acid). When finished, about 50 kilos. of slaked lime are added, the whole is well stirred, and the product run out on to flat iron trays which are placed in a retort (see Fig. 21, side view, and Fig. 22, section). The mass must be in thin layers. The retorts are strongly heated, and superheated steam is blown in to remove the naphthylamine as quickly as possible.* The cast iron coils from the retort are kept at 60°. The naphthylamine distils, with a little water, as a black oil which crystallises. It is mechanically separated from the water, melted in a preheater by means of a steam coil, and heated until free from water. It runs then into a wrought iron retort heated by direct fire. The retort is fitted with a sheet iron funnel on the top, to which part of the flue gases are led in order to prevent naphthylamine condensing in the upper part of the retort. The condenser to this retort is also kept surrounded with warm water. The naphthylamine distils as an almost water-white oil which is run into moulds and crystallises. The residues in the first retort are pyrophoric owing to the reaction between naphthylamine and iron oxide.

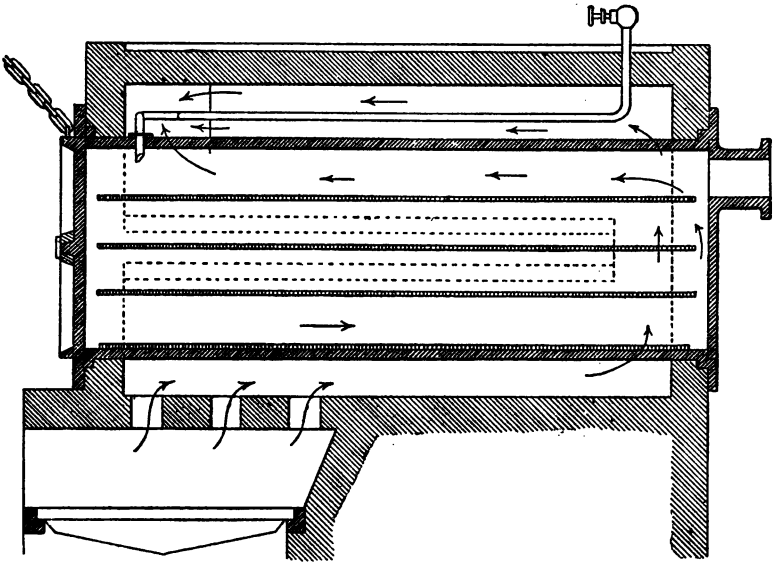


Fig. 21.

Paul, who carried out some small scale experiments with Witt's process (*Zeitsch. angew. Chem.*, 1897, **10**, 145), remarks that the water to be added to the iron and hydrochloric acid for the reduction should be ten times the weight of the hydrochloric acid. Repetition of Witt's process of nitration with 100 grams of naph-

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* The modern practice is to distil in a vacuum; it has also been proposed to separate the iron residues by means of an electromagnet (Chem. Fabrik Grünau, Landshoff, & Meyer, G.P., 83560, 184497), but this process has led to no practical results.

thalene gave a yield of 132 grams of nitronaphthalene, which is 98 per cent. of the theoretical. A large experiment with 1 kilo. gave the same result.

For the reduction 800 grams of sieved iron borings were mixed with 40 grams of hydrochloric acid (20·5° Bé., free from chlorine) and 400 grams of water; 656 grams of nitronaphthalene (91·5 per cent., setting point 50·5°) were added within three to four hours (20–25 grams every five minutes) at 80–85°, and the mixture was kept at this temperature for seven to eight hours. The whole product weighed 1·84 kilos. After distilling in a current of superheated steam, the naphthylamine weighed 406–418 grams.

Häussermann ("Die Industrie der Theerfarbstoffe," 1881) and Harmsen ("Die Fabrikation der Theerfarbstoffe," 1889), nitrate 10 parts of naphthalene with a mixture of 8 parts of nitric acid (D 1·4) and 10 parts of sulphuric acid. The temperature is raised gradually and very slowly to 70° and the mixture stirred for six hours longer at this point, after which the waste acid is drawn off from the molten nitronaphthalene.

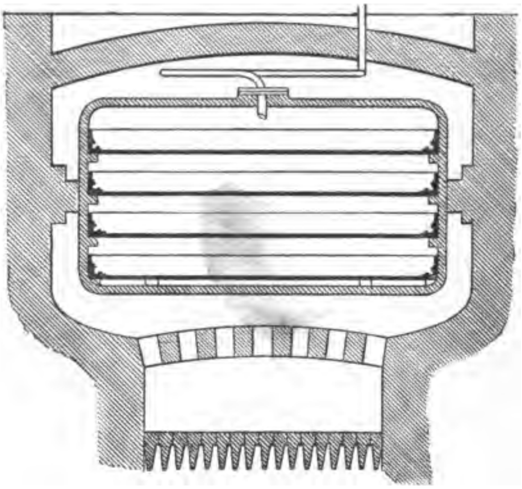

FIG. 22.

According to Grandmougin (*Rev. prod. chim.*, 1917, **20**, 196), 100 kilos. of naphthalene should give 125 kilos. of nitronaphthalene, and this quantity should yield 100 kilos. of α-naphthylamine.

α-Naphthylamine may be purified by heating it with 8–15 per cent. of xylene or solvent naphtha and allowing the mixture to cool and solidify. The mass is broken up and centrifuged, when a product is obtained having a solidifying point of 47–48°, whereas the crude product solidifies at 44–45°. From the expelled liquid the solvent is driven off, and the residue dissolved in warm dilute hydrochloric acid. On cooling, most of the α-naphthylamine is precipitated as hydrochloride and filtered off. From the filtrate the pure β-naphthylamine * is precipitated as sulphate by the addition of dilute sulphuric acid (Chemische Fabrik vorm. Weiler-ter-Meer, E.P., 16446 of 1907; F.P., 379985; G.P., 205076).

α-Naphthylamine melts at 51° and boils at 300°. Its specific gravity is 1·23 at 25°. One hundred grams of water at 15° dissolve 0·17 gram. α-Naphthylamine is used for making naphthylaminesulphonic acids, and for Sudan brown, Autol red, Sulphamine brown A, Double ponceau, Palatine red A, Fast reds, Crystal ponceau, Chromotrope 10B, Palatine black A, Neutral grey G, Coomassie wool blacks, Nyanza black B, Sulphone black, Sulphonecyanines (Tolyl blues), Naphthalene acid black 4B, Buffalo black 10B, Victoria black B, Jet black R, Naphthylamine black D (Buffalo black AD, Coomassie wool black D), Anthracite black, Naphthyl blue black, Naphthol black 6B (Acid black, Naphthol black 2B), Wool black B (Brilliant black B, Naphthol black OPAS, Buffalo black 2B), Diaminogen blue BB, Diaminogen BB, Diamond black F (Era black F, Fast chrome black B, Chrome fast black FRW), Diamond green, Biebrich patent blacks, Violet black, Naphthylene violet, Union brown A, Diazo blue black RS, Direct black V, Direct indone blue R, Benzo olive, Benzo grey, Benzo black blue G, 5G, and R, Benzo fast blue R, B, and Benzo indigo blue.

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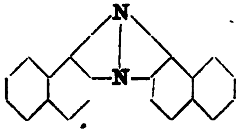
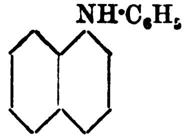
* The occurrence of β-naphthylamine in this reaction has also been observed by other authors, although Witt states definitely that β-nitronaphthalene is not produced at all in the nitration of naphthalene (compare, however, Thorpe's "Dictionary of Applied Chemistry" 1912, Vol. III., p. 580). As Doer (*Ber.*, 1870, 3, 291) obtained αβ-dinaphthazine,



by distilling α-nitronaphthalene with zinc dust, it seems possible that a little of this may be formed in the reduction, and may give β-naphthylamine by further action of the iron.

PHENYL-α-NAPHTHYLAMINE,



Phenyl-α-naphthylamine is formed by heating α-naphthylamine hydrochloride with aniline to 280° for about thirty-six hours (Girard and Vogt, *Compt. rend.*, 1871, **73**, 627; Streiff, *Annalen*, 1881, **209**, 152), but a more suitable method is to heat α-naphthol with aniline (Badische Anilin- & Soda-Fabrik, E.P., 2516 of 1880; F.P., 135547; G.P., 14612; Friedländer, *Ber.*, 1883, **16**, 2077; compare Ullmann and La Torre, *Ber.*, 1904, **37**, 2924).

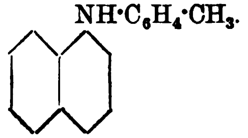
According to Katayama (*Kogyo-Kwagaku-Zasshi* [*J. Chem. Ind. Tokyo*], 1917, **20**, 353), a 64 per cent. yield of the theoretical is obtained as follows: An intimate mixture of α-naphthol (1 mol.), aniline (2 mols.), and calcium chloride (1 mol.) is heated in an autoclave for ten hours at 300°. The product is treated with boiling water to remove calcium chloride, with hydrochloric acid to remove uncombined aniline, and with sodium hydroxide solution to remove uncombined α-naphthol, and is then distilled in a vacuum in a current of carbon dioxide or hydrogen.

Knoll & Co. (G.P., 241853) claim an 85 per cent. yield of the theoretical by heating 143 parts of α-naphthylamine with 93 parts of aniline and 1 part of iodine for six hours at 230° and then for two hours at 250°. The product is washed with dilute hydrochloric acid and then with water, dried, and distilled in a vacuum, phenyl-α-naphthylamine passing over at 223°/10 mm.

Phenyl-α-naphthylamine melts at 62° and boils at 335°/258 mm. or 226°/15 mm.

It is used for making Jet black R, Sulphonazurine D, and Victoria blue B.

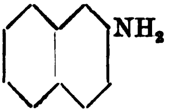
p-TOLYL-α-NAPHTHYLAMINE,



This is prepared in the same manner as phenyl-α-naphthylamine, using *p*-toluidine instead of aniline.

It melts at 78·5–79° and boils at 360°/528 mm. or 236°/15 mm. (Knoll & Co., *loc. cit.*, give 230°/10 mm.) It is used for making Night blue.

β-NAPHTHYLAMINE,



β-Naphthylamine is manufactured by heating together in an autoclave 100 parts of β-naphthol, 150 parts of ammonium sulphite (40 per cent.), and 100 parts of ammonia (20 per cent.) to 150° for some hours (Badische Anilin- & Soda-Fabrik, E.P., 1387 of 1900; F.P., 297464, 394820; G.P., 117471). The crude β-naphthylamine is filtered off, treated with sodium hydroxide to remove any unchanged β-naphthol, washed with water, and distilled in a vacuum to separate it from β-dinaphthylamine, which is always formed. The ammoniacal mother liquors are treated with lime and distilled to recover the ammonia.

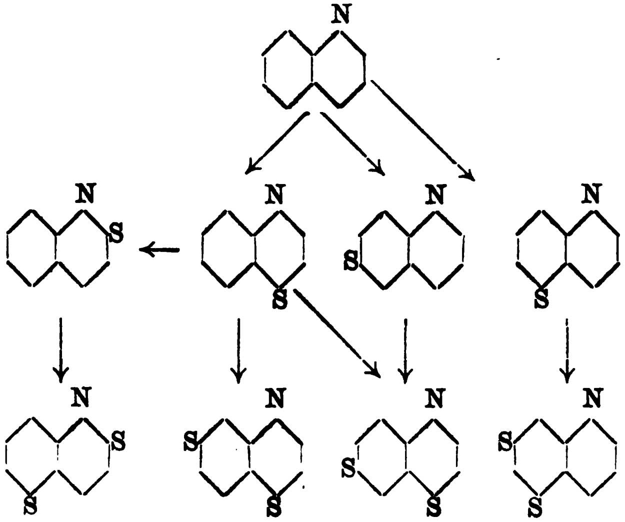
β-Naphthylamine melts at 112° and boils at 294°. The sulphate is more sparingly soluble than that of α-naphthylamine.

β-Naphthylamine is used for making β-naphthylaminesulphonic acids and for Sulphamine brown B, Azidine fast scarlets, Toluylene orange RR, Hessian purple N, and Naphthazurine B.

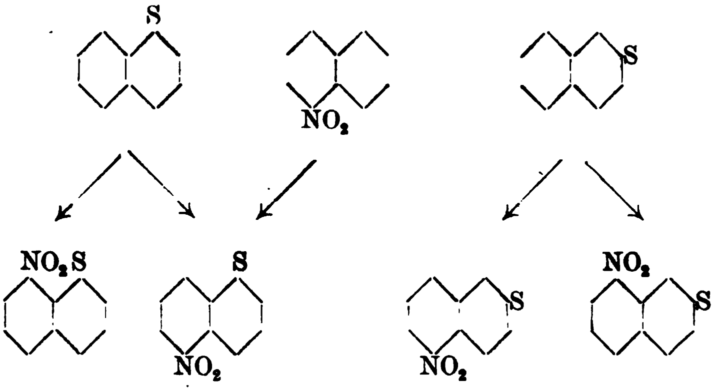
α-NAPHTHYLAMINESULPHONIC ACIDS.

Of the various methods of obtaining the sulphonic acids of α-naphthylamine, the two most important are (1) the sulphonation of α-naphthylamine, and (2) the reduction of α-nitronaphthalenesulphonic acids.

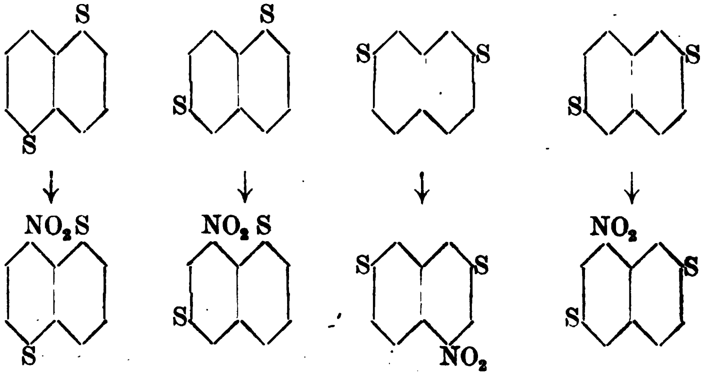
The acids produced by the first method are shown in the following scheme ($N = NH_2$ and $S = SO_3H$):



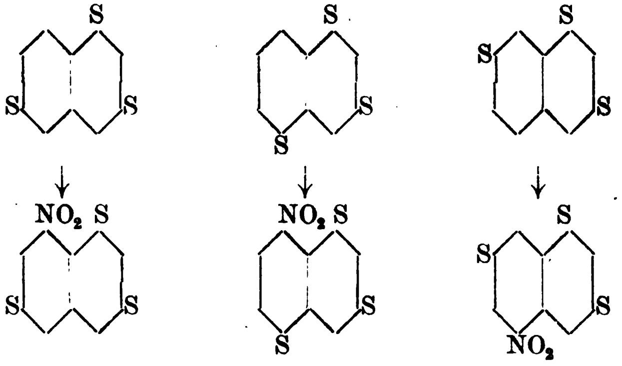
As regards the second method, α-nitronaphthalenemonosulphonic acids can be obtained (1) by sulphonating α-nitronaphthalene, (2) by nitrating naphthalene-α-sulphonic acid, and (3) by nitrating naphthalene-β-sulphonic acid. The acids obtained by these methods are indicated in the scheme below, which shows only the main products of the reactions :—



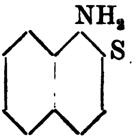
α-Nitronaphthalenedisulphonic acids are obtained by nitrating naphthalenedisulphonic acids as follows (main products only are shown) :—



Finally, the α-nitronaphthalenetrisulphonic acids are derived thus :



1-Naphthylamine-2-sulphonic Acid,

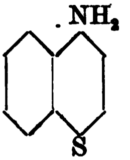


This acid is obtained by heating naphthionic acid (1-naphthylamine-4-sulphonic acid) with naphthalene (Farbenfabriken vorm. F. Bayer & Co., G.P., 72833). Twenty kilos. of dry, sieved, sodium naphthionate are added to 40–60 kilos. of molten naphthalene contained in a pan fitted with a stirrer and reflux condenser, and the mixture is heated to the boiling point of naphthalene (217°). The conversion takes two or three hours, at the end of which time the mass is cooled, water added, and the naphthalene distilled off in a current of steam. The residue is diluted with water to about 150–200 litres, neutralised with sodium carbonate, boiled, and filtered from a little dirt, and the solution treated with salt, causing the sodium 1-naphthylamine-2-sulphonate to precipitate.

The acid melts and decomposes at 262–265° and dissolves in 243 parts of water at 20° and 31·3 parts at 100° (Doliński, *Ber.*, 1905, 38, 1835). The sodium salt dissolves in 10 parts of boiling and 60 parts of cold water.

It is used for making Fast acid blue B.

Naphthionic Acid,



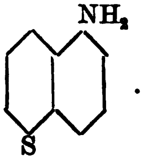
This is prepared from α-naphthylamine acid sulphate by the "baking" process (see Sulphanilic acid, p. 47), preferably in a vacuum. Fifty kilos. of α-naphthylamine are melted and added in a thin stream with good stirring to 36·5 kilos. of sulphuric acid (66° Bé.). The mixture is heated to 170–180° until a homogeneous mass is obtained, and then 2½ kilos. of oxalic acid are added. The mass foams up and, while still fluid, is run on to leaden trays and heated for eight hours at 170–180° in the oven. On cooling, the porous, grey mass is powdered, neutralised hot with milk of lime, filtered, and the residue washed until no further precipitate is obtained on adding hydrochloric acid to the filtrate. The acid is now precipitated by hydrochloric acid, filtered off, and dissolved in sodium carbonate or hydroxide, from which solution the sodium salt crystallises out. Should this still contain α-naphthylamine, it may be removed by washing with a little solvent naphtha. The yield is 64 kilos.

Naphthionic acid crystallises with $\frac{1}{2}H_2O$ and the sodium salt with $4H_2O$. The acid dissolves in 3,448 parts of water at 10°, 1,695 parts at 50°, and 438 parts at 100° (Doliński, *Ber.*, 1905, 38, 1835).

It is used for making 1-naphthol-4-sulphonic acid and 1-naphthylamine-4 : 6- and -4 : 7-disulphonic acids, and for Fast brown N, Fast reds, Azo rubine (Carmoisine, Chrome blue R), Diamond blue 3R, Azo red A, Croceine scarlet 3BX, Amaranth (Wool red), Cochineal red A (Brilliant scarlet S), Ponceau 6R, Chromotrope 8B, Clayton cotton brown, Fast brown, Congo red, Glycine red, Orange TA, Congo Corinth G (Buffalo garnet R), Congo rubine (Direct crimson B), Benzo orange R, Dianol red 2B, Benzopurpurine 4B and 10B, Brilliant purpurine 4B and R, Congo 4R, Congo Corinth B (Buffalo violet 4R), Azo violet, Azo Corinth, Benzo brown B, and Direct brown R (Toluylene brown R).

1-Naphthylamine-5-sulphonic Acid,

(Laurent's Acid)



Finely divided dry α-nitronaphthalene (20 parts) is added gradually to a mixture of sulphuric acid (35 parts) and fuming sulphuric acid (containing 24 per cent. of sulphur trioxide) (25 parts) at such a rate that the temperature does not rise above

90°, at which it is maintained for eight hours or until the sulphonation is complete. The product is poured on an equal weight of ice, when the 5-sulphonic acid is precipitated. The formation of dark, resinous substances, unavoidable when nitronaphthalene is sulphonated by fuming sulphuric acid, does not occur if fused salt is added to the acid in quantity sufficient to convert the dissolved sulphur trioxide into chlorosulphonic acid. Thus α-nitronaphthalene (10 parts) is added to the mixed sulphuric and chlorosulphonic acids obtained from 26 parts of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide) and the mixture heated at about 90° until sulphonation is complete (Erdmann, *Annalen*, 1888, **247**, 311). The product is poured on ice, filtered off, mixed with water, and reduced by adding iron borings. The mixture is neutralised with slaked lime, filtered, and the calcium salt in the filtrate converted into sodium salt by means of sodium carbonate. The solution may be used direct or the acid precipitated by acidifying.

The acid may also be prepared by sulphonating α-naphthylamine.

Finely powdered, dry α-naphthylamine hydrochloride is added gradually to about 2 parts of well cooled (with ice or snow) fuming sulphuric acid (containing 20–25 per cent. of sulphur trioxide), whereby the salt dissolves with the evolution of hydrogen chloride. The quantity of α-naphthylamine hydrochloride is so adjusted that a little free sulphur trioxide is present at the end of the operation. The product is poured on ice, the acid filtered off, washed, and converted into the calcium salt, from which either the sodium salt or the free acid is obtained. The acid, prepared in this way, contains a little naphthionic acid, and in order to separate this, the solution of the calcium salt is evaporated until the calcium salt of the 1 : 5-acid separates out, the calcium salt of naphthionic acid remaining in the mother liquors.

Probably the most convenient method of preparation is by nitrating naphthalene-α-sulphonic acid and reducing the nitro-acids, which process yields, as chief product, 1-naphthylamine-8-sulphonic acid; this is easily separated from the 5-sulphonic acid, the process being described on p. 193.

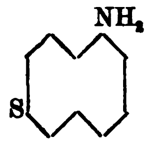
The acid crystallises in anhydrous needles soluble in about 940 parts of cold water.

The sodium salt crystallises with $1H_2O$ and is readily soluble in water.

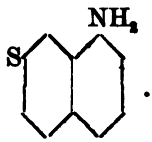
It is used for making Brilliant fast red G, Sulphoncyanine black B, Diazo black B, Benzopurpurine 6B, Congo brown R, and 1-naphthol-5-sulphonic acid by the diazo-reaction.

1-Naphthylamine-6- *and* -7-sulphonic Acids,

(Cleve's Acids)



and



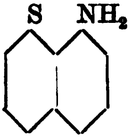
Two hundred and thirty kilos. of sodium naphthalene-β-sulphonate are dissolved in 1,150 kilos. of sulphuric acid, the temperature not being allowed to rise above 30°. The mixture is cooled to 0° and a mixture of nitric and sulphuric acids containing 70 kilos. of nitric acid (reckoned as 100 per cent.) are added at 0–10°. The formation of the nitro-acid is complete after a few hours (Cassella & Co., E.P., 6972 of 1891, addition to F.P., 210950; G.P., 67017). The mixture is then blown into water, neutralised with slaked lime, and filtered, the wash-water being used in the next batch. The solution of calcium salts is reduced with iron borings and a little acetic acid, the product rendered alkaline with a little slaked lime, and filtered from the iron. The filtrate is either treated with sodium carbonate and the solution of sodium salts used direct, or it is evaporated and acidified, when, on cooling, the solid acids are obtained.

1-Naphthylamine-6-sulphonic acid crystallises anhydrous or with $2H_2O$ and dissolves in 1,000 parts of water at 16°. The sodium salt crystallises with $4\frac{1}{2}H_2O$.

1-Naphthylamine-7-sulphonic acid crystallises with $1H_2O$ and dissolves in 220 parts of water at 25°. The sodium salt crystallises with $\frac{1}{2}H_2O$.

The mixture of acids (accompanied by a trace of the 3-sulphonic acid which is formed in their preparation) is used for making 1 : 4-naphthylenediamine-6-sulphonic acid, and for sulphone black G,R, Naphthalene acid black 4B, Granite black, Sulphoncyanine black B, 2B, Carbon blacks (Naphthamine direct blacks), Anthracene acid blacks, Biebrich patent blacks, Columbia blacks and Anthracene acid brown B.

1-NAPHTHYLAMINE-8-SULPHONIC ACID,
(S ACID; PERI ACID)

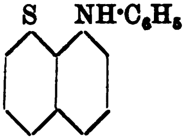


One hundred parts of sieved naphthalene are added quickly to 300 parts of sulphuric acid at 60°, the whole being very thoroughly stirred. The mixture is cooled and 84 parts of nitric acid (D 1·4) are run in, the temperature not being allowed to rise above 40°. After being stirred for a few hours, the product is poured into ice-water, neutralised with slaked lime, filtered from the gypsum, and the solution of the calcium salts of the nitro-acids is slightly acidified with sulphuric acid and then reduced by means of 156 parts of iron borings; the reduction requires about four hours. Sodium carbonate is now added to precipitate iron and to form the sodium salts (about 42 parts) and the whole filtered. The filtrate is evaporated until it is almost solid (40° Tw.). When cold, the sodium 1-naphthylamine-8-sulphonate is filtered off (53 parts) and the filtrate, on acidification, yields the 5-sulphonic acid (20 parts). The latter is purified by dissolving it in sodium hydroxide, filtering after some time from a little of the sodium salt of the 8-sulphonic acid, and precipitating with hydrochloric acid, when about 18 parts are obtained.

In the patents describing the preparation of this acid (Schoellkopf Aniline and Chemical Co., E.P., 15775 and 15781 of 1885; F.P., 173083, 173084; G.P., 40571; U.S.P., 333034), 100 parts of calcium naphthalene-α-sulphonate are mixed with 200 parts of sulphuric acid, and then 45 parts of nitric acid (40° Bé.) added at 90–100°, the further operations being as described above.

1-Naphthylamine-8-sulphonic acid crystallises with $1H_2O$ and dissolves in 4,800 parts of water at 21° and 238 parts of boiling water. The sodium salt is anhydrous and dissolves in 885 parts of water at 24°, or 375 parts at 100°. The acid is used for making 1-naphthylamine-4 : 8-disulphonic acid.

1-PHENYLNAPHTHYLAMINE-8-SULPHONIC ACID,



(1) One part of 1-naphthylamine-8-sulphonic acid, 3·5 parts of aniline, and 1 part of aniline hydrochloride are heated in an autoclave for ten hours at 160–170°. After cooling, the mixture is treated with dilute hydrochloric acid and the phenylated acid filtered off. This is redissolved in sodium carbonate solution and boiled to expel traces of aniline, the solution filtered, and acidified with hydrochloric acid. The acid may be purified through the calcium salt. The separation of aniline is probably more completely effected by adding sodium carbonate to the cold autoclave mixture and distilling off the aniline in a current of steam.

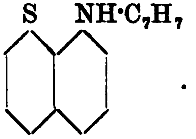
Good results are also obtained by using a mixture of 1 part of 1-naphthylamine-8-sulphonic acid, 2–4 parts of aniline, and 0·1 part of benzoic acid (Farbenfabriken vorm. F. Bayer & Co., E.P., 7337A of 1892; G.P., 70349).

(2) 98·2 Kilos. of 1-naphthylamine-8-sulphonic acid are suspended in boiling water, 270 kilos. of aniline are added, and dissolved by 150 kilos. of hydrochloric acid (22° Bé.). The mixture is heated in an autoclave for twenty hours at 140°. On cooling, it is rendered alkaline with sodium carbonate, diluted with water, and the excess of aniline distilled off with steam. The liquid is filtered and the phenylated acid is salted out (Kalle & Co., E.P., 12326 of 1901; F.P., 311838; G.P., 170630).

(3) Thirty-three parts of the sodium hydrogen salt of 1-naphthylamine-4 : 8-disulphonic acid are added to 130 parts of aniline and the mixture is heated at 180° for thirty hours. It is then rendered alkaline with sodium carbonate, the excess of aniline distilled off by a current of steam, the solution cooled, filtered, and the 1-phenylnaphthylamine-8-sulphonic acid is precipitated by acid. In this process, benzoic acid or aniline hydrochloride may be added to the above mixture (Aktiengesellschaft für Anilinfabrikation, E.P., 15624 of 1904; F.P., 344810; G.P., 158923).

The acid is sparingly soluble in water, but the sodium salt is readily soluble. It is used for making Sulphone acid blue R, Sulphone black, and Coomassie Navy blues (Sulphoncyanines, Tolyl blue).

1-*p*-Tolylnaphthylamine-8-sulphonic Acid,



(1) Ten kilos. of 1-naphthylamine-8-sulphonic acid and 40 kilos. of *p*-toluidine are heated in an autoclave for ten hours at 140–150°. The *p*-tolyl acid is worked up just as in the case of the phenylated acid (see preparation 1, p. 194). (Farbenfabriken vorm. F. Bayer & Co., E.P., 7337A of 1892 ; G.P., 71168.)

(2) 49·1 Kilos. of the 1 : 8-acid (91 per cent.) are suspended in 400 litres of hot water, 150 kilos. of *p*-toluidine are added, and dissolved by 100 kilos. of hydrochloric acid (22° Bé.) ; the mixture is heated for fifteen hours at 150°. On cooling, it is rendered alkaline with 60 kilos. of sodium carbonate, diluted with 250 litres of water, and the excess of *p*-toluidine is removed by a current of steam. The liquid is filtered and may be used direct for making azo-dyes, or the *p*-tolyl acid can be salted out. The charge can also be boiled in an open vessel under a reflux condenser, but this process requires a much longer time (Kalle & Co., E.P., 12326 of 1901 ; F.P., 311838 ; G.P., 170630).

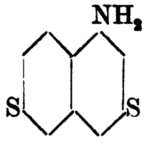
(3) Thirty-three parts of the 1 : 8-acid, 200 parts of *p*-toluidine, and 1·6 parts of benzoic acid are heated in an autoclave for thirty hours at 190°. The further working up is as described for the corresponding phenylated acid (preparation 3, p. 194).

The acid is sparingly soluble in water, but the sodium salt is readily soluble.

It is used for making Sulphone acid blue B and Coomassie Navy blues (Sulphoncyanines).

1-Naphthylamine-3 : 6-disulphonic Acid,

(Freund's Acid)



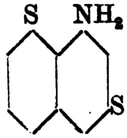
This can be prepared by the nitration and reduction of naphthalene-2 : 7-disulphonic acid, or the sulphonation mixture, containing also the 2 : 6-acid, is nitrated direct. Freund (E.P., 1069 of 1883; F.P., 153847; G.P., 27346) gives the following directions: Twenty kilos. of naphthalene are heated with 100 kilos. of concentrated sulphuric acid for eight to ten hours at 160–200°; the mixture is cooled and 40 kilos. of nitric acid (50 per cent.) or the corresponding amount of a nitrate are added, care being taken that the temperature does not rise too high. After being stirred for some hours, the mass is poured into 200 litres of water and reduced with iron borings. The product is neutralised with milk of lime and the solution of the calcium salts is concentrated by evaporation.

Alternatively, 33 kilos. of sodium naphthalene-2 : 7-disulphonate are dissolved in 50 kilos. of concentrated sulphuric acid, and 25 kilos. of nitric acid, or the corresponding amount of a nitrate, are added slowly. The product is then reduced and worked up as above.

According to Kalle & Co. (G.P., 233934), 9·5 kilos. of the acid sodium salt of 1-naphthylamine-3 : 6 : 8-trisulphonic acid (p. 202) containing 90 per cent. of diazotisable acid are boiled with 7·5 kilos. of sodium hydroxide solution, 3 kilos. of zinc dust, and 90 litres of water for seven hours under a reflux condenser. The excess of sodium hydroxide is neutralised with hydrochloric acid, the solution filtered from zinc oxide, and acidified, when the acid sodium salt of 1-naphthylamine-3 : 6-disulphonic acid is precipitated.

The acid is easily soluble in water, and the acid sodium salt crystallises with $3H_2O$ and is also readily soluble. It is used for making the corresponding naphthol acid and for Naphthylamine black D and Anthracite black.

1-NAPHTHYLAMINE-3 : 8-DISULPHONIC ACID, (ε-ACID)



This is obtained, together with 1-naphthylamine-4 : 8-disulphonic acid, when a mixture of naphthalene-1 : 5- and -1 : 6-disulphonic acids (see pp. 176–177) is nitrated and the mixture of nitro-acids reduced. The product of the interaction of 100 kilos. of naphthalene and 280 kilos. of fuming sulphuric acid, as described by Paul (*loc. cit.*), is cooled to about 30°, and 100 kilos. of nitric acid (40° Bé.) are run in slowly within eighteen hours, the temperature being kept at 20–30°. In the meantime, 170 kilos. of lime are slaked with about 1,000 litres of water and run into a tub set at a lower level than the sulphonation pan. The nitration mixture is run into this (or is blown into it if there is no run-off pipe), care being taken that an alkaline reaction is always present. The mixture is heated to boiling, filtered through a filter press, and the gypsum stirred up with hot water and filtered again. The wash-waters are used in the next batch. The calcium salts of the nitro-acids are converted into sodium salts and the solution is evaporated in an iron pan to about 1,500 litres.

Reduction.—The evaporated solution is run into a tub of about 2,000 litres capacity, fitted with a stirrer, heated to boiling, and 200 kilos. of iron borings are added during half-an-hour. Into the mixture 100 kilos. of sulphuric acid (66° Bé.) are run slowly during 2½ hours, and after two to three hours 20 kilos. more iron are added if necessary. The solution should then have lost its yellow colour and become pale brown. The reduced liquor is neutralised with slaked lime, filtered, the gypsum and iron residue washed, and the calcium salts are converted into sodium salts. In order to separate the two isomeric acids, the liquor is evaporated in an iron pan until it shows 28° Bé., and, after eight days, the sodium salt of the 4 : 8-disulphonic acid will have crystallised out. This is filtered, pressed, and recrystallised if necessary (see p. 200). The filtrate is treated with 1,000 litres of water, 600 kilos. of salt, and 480 kilos. of hydrochloric acid and then shows 28° Bé. After some time, the crude acid sodium salt of the 3 : 8-acid crystallises out and is recrystallised by the aid of salt. The final filtrate contains the 2-naphthylamine-disulphonic acids, which are not worked up. The yield of each of the 1-naphthylaminedisulphonic acids is about 20 per cent. (compare also E.P., 4625 of 1888 ; F.P., 189712 ; G.P., 45776, 52724 ; U.S.P., 405938 ; *Ber.*, 1889, **22**, 3328 ; 1890, **23**, 77). The acid is obtained free from the 4 : 8-disulphonic acid when the mixture obtained by Paul's method of preparation of naphthalene-1 : 6-disulphonic acid (p. 177) is nitrated and reduced. The product of the interaction of 200 kilos. of the naphthalene-β-sulphonic acid mixture and 400 kilos. of sulphuric acid is cooled to 25° and 85 kilos. of nitric acid (40° Bé.) are added at 25–30°. The product is neutralised with slaked lime and filtered as usual. To the filtrate (2,000 litres) are added 200 kilos. of iron borings and then 100 kilos. of sulphuric acid diluted with an equal bulk of water. When the reduction is finished, the mixture is neutralised with slaked lime, the filtrate converted into sodium salt, and the solution acidified and treated with common salt.

The concentration is kept so that the mixture shows 26° Bé. when the acid sodium salt of the 3 : 8-disulphonic acid separates. The yield is about 27–30 per cent. of the theoretical. The salt may be purified as described above.

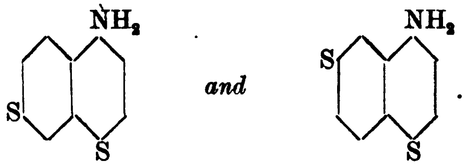
Small scale experiments by Paul (*loc. cit.*) showed that the nitro-acid can be isolated by pouring the nitration mixture into salt solution. If the paste is now reduced in acid solution with zinc dust, the acid zinc salt separates out and can be purified by solution in water and acidification with sulphuric acid, whereby the acid zinc salt is obtained pure.

The acid crystallises with $3H_2O$ and is readily soluble in water. The normal sodium salt crystallises with $6H_2O$ and is very readily soluble in water; the acid sodium salt crystallises with $2H_2O$ and dissolves in about 30 parts of cold water.

It is used for making the corresponding naphthol acid.

1-NAPHTHYLAMINE-4 : 6- *and* -4 : 7-DISULPHONIC ACIDS,

(DAHL'S ACIDS II AND III)



One hundred kilos. of ground and sieved naphthionic acid are added slowly to 350 kilos. of fuming sulphuric acid (containing 25 per cent. of sulphur trioxide), the temperature not being allowed to rise above 30°. After two to three days' stirring at this temperature, 6 drops of the mixture are added to 10 c.c. of water, and if, after five to six hours, no precipitate has formed, the sulphonation is finished. It is now poured into water, neutralised with milk of lime, the gypsum filtered off, and the solution of calcium salts evaporated to dryness. The dried salts are ground and sieved and extracted with ten times their quantity of 85 per cent. alcohol. The residue, which consists of the 4 : 7-disulphonic salt (70 per cent.), is dried and converted into the sodium salt. The filtrate, which contains the 4 : 6-disulphonic salt (30 per cent.), is evaporated, and the calcium salt converted into the sodium salt. The free acids can be obtained by acidifying the solution of the sodium salts (Dahl & Co., G.P., 41957).

The diluted sulphonation mixture may also be treated with solid potassium chloride, whereby the acid potassium salt of the 4 : 7-disulphonic acid is precipitated.

The 4 : 7-disulphonic acid is also obtained by the action of sodium hydrogen sulphite on 1 : 8-dinitronaphthalene.

Sixteen kilos. of this compound in the form of a paste containing about 50 per cent. of water are added to a mixture of 150 kilos. of sodium hydrogen sulphite (40 per cent.) and 30 kilos. of 25 per cent. ammonia. The mixture is warmed to 80–90° and after eight hours it is filtered, 60 kilos. of hydrochloric acid are added to the filtrate and the whole is stirred for half a day, when a voluminous precipitate is formed. This is filtered off and the press-cake dissolved in 100 litres of warm water. On cooling, 1-naphthylamine-4 : 7-disulphonic acid crystallises out and is filtered off. On adding 25 kilos. of salt to the filtrate, 1-naphthylamine-2 : 4 : 7-trisulphonic acid is obtained (Farbwerke vorm. Meister, Lucius, & Brüning, G.P., 215338).

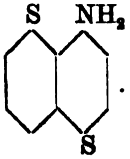
The technical mixture of 1 : 5- and 1 : 8-dinitronaphthalene may also be used. Thus, 200 kilos. of a 60 per cent. paste are warmed for five to six hours at 80–90° with 740 kilos. of sodium hydrogen sulphite (40 per cent.) and 140 kilos. of 25 per cent. ammonia. The residual 1 : 5-dinitronaphthalene (30–35 kilos.) is filtered off and the filtrate worked up as above (*idem*, G.P., 221383). A process for obtaining the 4 : 6-disulphonic acid consists in boiling a mixture of 9·5 kilos. of the acid sodium salt of 1-naphthylamine-4 : 6 : 8-trisulphonic acid (p. 202), 7·5 kilos. of sodium hydroxide solution, 3 kilos. of zinc dust, and 90 litres of water for seven hours under a reflux condenser. The excess of sodium hydroxide is neutralised with hydrochloric acid, the solution filtered from the zinc oxide, and acidified, when the acid sodium salt of 1-naphthylamine-4 : 6-disulphonic acid is precipitated (Kalle & Co., G.P., 233934).

The normal sodium salt of 1-naphthylamine-4 : 6-disulphonic acid is readily soluble in water, whilst the acid sodium salt dissolves in 6 parts of water at 20°.

The normal sodium salt of the 4 : 7-disulphonic acid crystallises with $3H_2O$ and is readily soluble in water ; the acid sodium salt is soluble in 140 parts of water at 20° or 20 parts at the boiling point.

The mixed acids are used for making Archil substitute (Apollo red), Naphthyl blue black, Naphthol black 6B (Acid black), and (the 4 : 7-acid) Phenylene black.

1-Naphthylamine-4 : 8-disulphonic Acid,
(δ-Acid ; Disulpho-acid S)



This is produced, together with 1-naphthylamine-3 : 8-disulphonic acid, when a mixture of naphthalene-1 : 5- and-1 : 6-disulphonic acids (see p. 196) is nitrated and the mixture of nitro-acids reduced. The operation is described on p. 196.

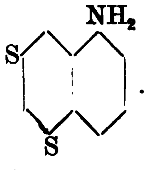
The crude sodium 1-naphthylamine-4 : 8-disulphonate is purified by dissolving 50 kilos. of the paste (= 36 kilos. of 100 per cent.) with water to about 190 litres, cooling to about 40°, and filtering from any admixed monosulphonic acid (1-naphthylamine-8-sulphonic acid formed from any naphthalene-α-sulphonic acid that may have escaped sulphonation). The filtrate is treated with 18 kilos. of hydrochloric acid, and after some time the acid sodium salt separates out.

It is also obtained by treating 1-naphthylamine-8-sulphonic acid with three times its weight of fuming sulphuric acid (containing 10 per cent. of sulphur trioxide), at first in the cold and afterwards at 100°. The product is neutralised with milk of lime and the calcium salt converted into the sodium salt in the usual way. (Schöllkopf Aniline and Chemical Co., E.P., 15775 and 15781 of 1885 ; F.P., 173083, 173084 ; G.P., 40571 ; U.S.P., 333034).

The normal sodium salt crystallises with $2H_2O$ and is readily soluble in water ; the acid sodium salt is sparingly soluble in cold water.

It is used for making 1-amino-8-naphthol-4-sulphonic acid, 1 : 8-dihydroxynaphthalene-4-sulphonic acid, and 1 : 8-naphthasultam-2 : 4-disulphonic acid.

1-Naphthylamine-5 : 7-disulphonic Acid,

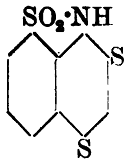


This is prepared by sulphonating the acetyl compound of 1-naphthylamine-5-sulphonic acid or of α-naphthylamine. Five parts of 1-naphthylamine-5-sulphonic acid, 30 parts of glacial acetic acid, 3 parts of anhydrous sodium acetate, and 5 parts of acetic anhydride are boiled together under reflux for eight hours or until a sample cannot be diazotised. The mixture is then heated on an oil-bath and the acetic acid and acetic anhydride are distilled over; the residue is dried. It is then mixed with 40 parts of fuming sulphuric acid (containing 30 per cent. of sulphur trioxide) at 0–5° and the mixture kept at 20–30° for twelve to fifteen hours or until a sample, on diluting, boiling, and then cooling, does not show any separation of monosulphonic acid. The sulphonation is poured on 80 parts of ice, the mixture boiled for half-an-hour so as to hydrolyse the acetyl acid, and, on cooling, the precipitated acid sodium salt is filtered off.

Alternatively, aceto-α-naphthalide is added to 5 parts of fuming sulphuric acid (containing 35 per cent. of sulphur trioxide) at 0–5°, the temperature is maintained at 25–30° for twenty to twenty-four hours, and the product poured on 10 parts of ice, the solution being boiled and then saturated with salt, when, on cooling, the acid sodium salt separates (Badische Anilin- & Soda-Fabrik, E.P., 2370 of 1893; G.P., 69555; Cassella & Co., G.P., 188505).

The acid sodium salt, $NaH_3A_2 + 5H_2O$, forms very soluble needles. It is used for making 1-amino-5-naphthol-7-sulphonic acid.

1 : 8-NAPHTHASULTAM-2 : 4-DISULPHONIC ACID,



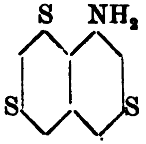
Three hundred parts of the acid sodium salt of 1-naphthylamine-4 : 8-disulphonic acid (p. 200) are gradually added to 600 parts of fuming sulphuric acid containing 40 per cent. of sulphur trioxide. The solution is warmed to 80–90°, when the mass solidifies. Heating is continued until a sample diluted with water does not form a diazo-compound and gives no dye on the addition of diazobenzenesulphonic acid (diazotised sulphanilic acid). The batch is then poured into ice-water, neutralised with milk of lime, the gypsum filtered off, the calcium salt converted into sodium salt, and the solution evaporated to dryness (Farbenfabriken vorm. F. Bayer & Co., E.P., 4979 of 1893; G.P., 79566, 80668; Aktiengesellschaft für Anilinfabrikation, E.P., 2984 of 1893; F.P., 228397; G.P. Anm. A., 3346; Dressel and Kothe, *Ber.*, 1894, **27**, 2139).

The corresponding 1-naphthylamine-2 : 4 : 8-trisulphonic acid is unknown.

The disodium salt crystallises with $2H_2O$ and the trisodium salt with $8\frac{1}{2}H_2O$, both being readily soluble in water.

It is used for making 1-amino-8-naphthol-2 : 4-disulphonic acid.

1-Naphthylamine-3 : 6 : 8-trisulphonic Acid,

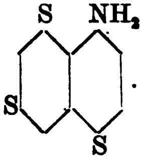


The sulphonation mixture containing naphthalene-1 : 3 : 6-trisulphonic acid (p. 181) is treated with the calculated quantity of nitric acid, the temperature being kept at about 25–30°. The nitration mixture is then blown into water in a tub, and iron borings are added, the reduction being carried out at about 50°. After the reduction is finished, the batch is filtered and saturated with salt, whereby the disodium salt of 1-naphthylamine-3 : 6 : 8-trisulphonic acid separates out completely (Heumann, "Die Anilinfarben," II., 539), and is filtered off (Koch, E.P., 9258 of 1890; G.P., 56058).

The disodium salt is readily soluble in water but insoluble in saturated salt solution, and the readily soluble trisodium salt crystallises with $3H_2O$.

It is used for making 1-amino-8-naphthol-3 : 6-disulphonic acid (H acid).

1-Naphthylamine-4 : 6 : 8-trisulphonic Acid,



Naphthalene-1 : 3 : 5-trisulphonic acid as produced by sulphonating sodium 1 : 5-disulphonate (p. 180) is, while still in the sulphonation mixture, mixed with such a quantity of ice that the liquid has a specific gravity corresponding with 63–66° Bé. at 15°. The liquid is cooled to 5° and the calculated quantity of nitric acid (namely, 1 molecular proportion of nitric acid for 1 molecular proportion of the naphthalenedisulphonic acid used), mixed with sulphuric acid, is stirred into it at 5–10°. It is then poured into water and the liquid neutralised with slaked lime; the precipitated calcium sulphate is filtered off, and the filtrate is diluted with water and reduced with iron borings and a little acid. When reduction is complete, the liquid is rendered alkaline with milk of lime, the precipitate filtered, the calcium salt converted into sodium salt, and the filtrate evaporated. On acidifying the concentrated solution, the acid sodium salt is obtained. (Farbenfabriken vorm. F. Bayer & Co., E.P., 17141C of 1893; F.P., 237872; G.P., 80741; U.S.P., 563382).

The method used by Kalle & Co. (E.P., 515 of 1894; G.P., 93700, 99164; U.S.P., 563383, 563384) consists in adding to the cold sulphonation mixture containing naphthalene-1 : 3 : 5-trisulphonic acid (see Kalle's method of preparation), prepared from 10 parts of sodium naphthalene-1 : 5-disulphonate, 9·2 parts of a mixture of sulphuric and nitric acids (containing 25 per cent. of the latter) at a temperature not above 60°. The mixture is stirred for a short time, poured into five times its quantity of water and reduced with iron borings. The reduction mixture is neutralised with slaked lime, filtered, and the calcium salt converted into sodium salt. On acidifying the solution the acid sodium salt of 1-naphthylamine-4 : 6 : 8-trisulphonic acid crystallises out.

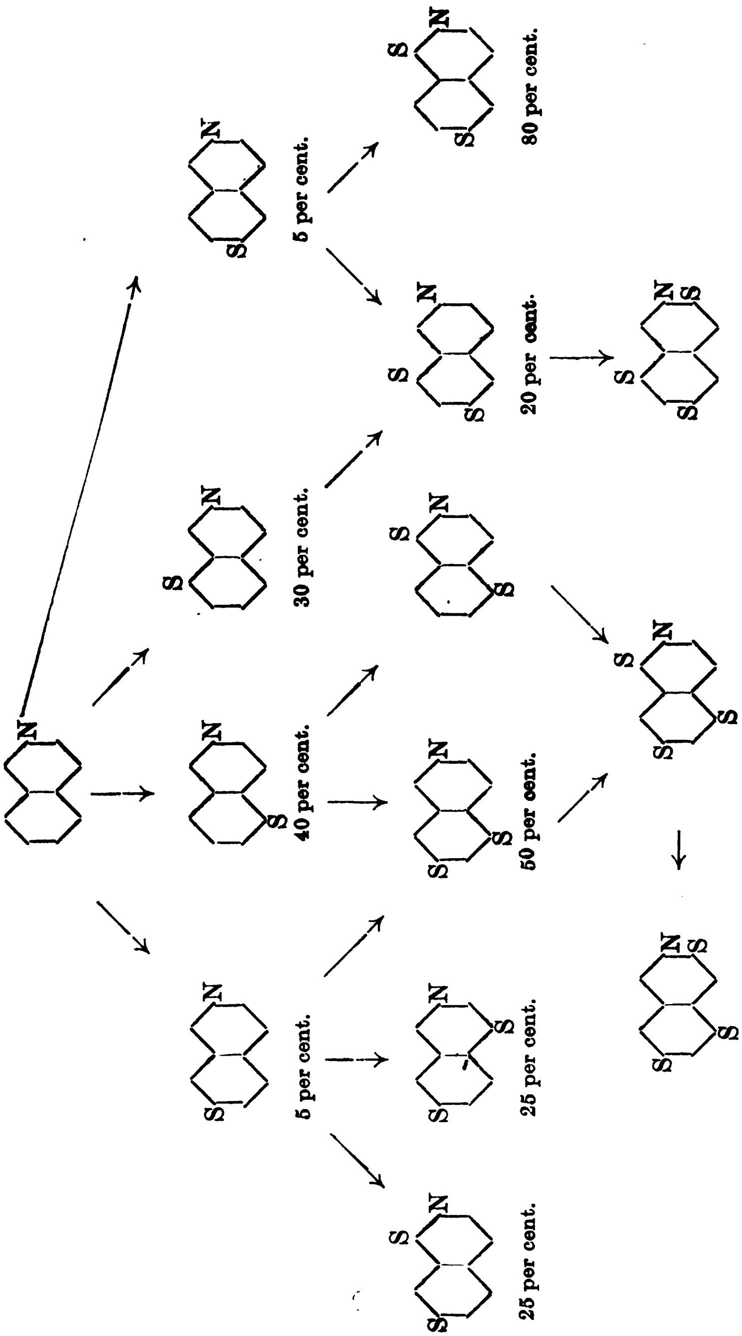
The acid is used for making 1-amino-8-naphthol-4 : 6-disulphonic acid (K acid).

β-Naphthylaminesulphonic Acids.

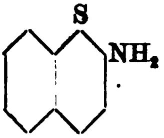
β-Naphthylaminesulphonic acids are obtained (1) by the sulphonation of β-naphthylamine or of the derived β-naphthylaminesulphonic acids, or (2) by heating the sodium salts of the corresponding β-naphtholsulphonic acids with ammonium hydrogen sulphite solution and ammonia at 100–150°. The process is applicable to all acids which do not contain a 4-sulphonic acid group, and is of value for the production of the 6-, or 7-, or 8- monosulphonic acid, as each of the corresponding β-naphtholsulphonic acids is obtained in a pure state much more easily from β-naphthol than is the β-naphthylaminesulphonic acid from the mixed acids produced in the sulphonation.

A careful study of the mechanism of the sulphonation of β-naphthylamine has been made by Green and Vakil (*Trans.*, 1918, **113**, 35).

The following scheme shows the production of sulphonic acids by the first method ($N = NH_2$ and $S = SO_3H$), and the relative amounts produced are indicated in percentages.


5 per cent.
80 per cent.
30 per cent.
20 per cent.
40 per cent.
50 per cent.
5 per cent.
25 per cent.
25 per cent.
N
S

2-Naphthylamine-1-sulphonic Acid,



This is obtained by heating 50 kilos. of sodium 2-naphthol-1-sulphonate with 200–250 kilos. of ammonia (15–20 per cent.) in an autoclave at 220–230° for twenty hours, or the same weight of sodium salt is heated with a solution of 30 kilos. of ammonium chloride in 200–250 kilos. of ammonia (15 per cent.) for ten to twelve hours at 200–210°.

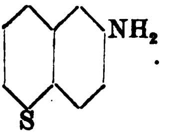
After driving off the ammonia and cooling again, the solution is filtered from β-naphthylamine and the acid precipitated by adding hydrochloric acid, or obtained as sodium salt by salting out the solution after concentration by evaporation. A little unattacked naphtholsulphonic acid may be recovered from the filtrate by adding more salt or by making the basic barium salt. In the latter form it may be precipitated from the solution of the naphthylamine acid (Tobias, E.P., 15404 of 1893; F.P., 232467; G.P., 74688).

The formation of β-naphthylamine can be avoided if the naphtholsulphonate is heated with 40 per cent. ammonium hydrogen sulphite solution and 20 per cent. ammonia at 100–150° until the reaction is complete (see under β-Naphthylamine, p. 187), and the product afterwards acidified.

The acid is sparingly soluble in water, whilst the sodium salt crystallises with $1H_2O$ and is readily soluble.

It is used for making Lithol red R and Lake Bordeaux B.

2-Naphthylamine-5-sulphonic Acid,



Eighty-five kilos. of β-naphthylamine sulphate are gradually added to 270 kilos. of sulphuric acid and stirred in a closed pan at 15–20° until a sample gives a clear solution in dilute ammonia (48–70 hours). The product contains about 55 per cent. of the 5-sulphonic acid and only traces of the 6-acid. It is poured into water, the precipitated acids filtered off and converted into sodium salts, which are dried and extracted with six times their quantity of alcohol (90–95 per cent.). The sodium salt of the

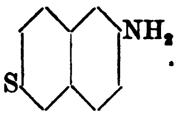
8-sulphonic acid is insoluble, whilst about half the original quantity dissolves. The alcoholic solution is distilled, the sodium salts are dissolved in water, and the acids precipitated by adding hydrochloric acid. They are converted into the barium salts by boiling with barium carbonate, and, on cooling, the barium salt of the 6-sulphonic acid separates out and is filtered off. The solution, on acidification with hydrochloric acid, deposits the 5-sulphonic acid, which is filtered off and may be converted into the sodium salt (Dahl & Co., E.P., 7712 of 1884; G.P., 29084, 32271, 32276).

The acid dissolves in 260 parts of boiling or 1,300 parts of cold water.

The sodium salt crystallises with $5H_2O$ and is very readily soluble in water; it dissolves in 10 parts of boiling alcohol (95 per cent.).

It is used for making β-naphthylamine-5 : 7-disulphonic acid.

2-NAPHTHYLAMINE-6-SULPHONIC ACID, (BRÖNNER'S ACID.)



This is prepared from 2-naphthol-6-sulphonic acid by the action of ammonia. In the first patent (Farbenfabrik vorm. Brönner, E.P., 3724 of 1882; F.P., 150503; G.P., 22547; U.S.P., 332829), 60 kilos. of the neutral or acid ammonium salt of Schaeffer acid are heated with 12 kilos. of calcium hydroxide (or 20 kilos. of sodium carbonate) and 60 kilos. of water for twenty-four hours at 180–200° in an autoclave. The mass is dissolved in 50 litres of hot water,* and the solution filtered, if necessary, acidified and the amino-acid filtered off.

A method described by Landshoff (G.P., 27378) consists in passing a stream of ammonia over the sodium salt of Schaeffer acid at 200–250° for about twelve hours, but a more satisfactory method is to heat the sodium salt of Schaeffer acid with concentrated aqueous ammonia at 180°. By far the best method, however, is to heat the sodium salt (50 parts) with 75 per cent. ammonium sulphite solution (8 parts) and 20 per cent. ammonia (74 parts) at 200° for six hours (see under β-Naphthylamine, p. 187), the product being afterwards acidified.

The acid is also obtained, mixed with a little of the 7-sulphonic acid, when a mixture of equal molecules of β-naphthylamine and

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* The United States patent gives 500 litres.

sulphuric acid is baked at 200–210° for two hours and the product powdered and converted into the sodium salt (Liebmann, G.P. Anm. L., 3205).

The acid crystallises with $1H_2O$ and dissolves in 630 parts of boiling water. The sodium salt crystallises with $2H_2O$ and dissolves in about 40 parts of cold water.

It is used for making Double brilliant scarlet G, Double scarlet extra S, Chrome yellow (Milling yellow), Cloth red 3G extra, Hessian brilliant purple, Benzopurpurine B, Brilliant purpurine 4B, Brilliant Congo R, and Dianol red B.

2-NAPHTHYLAMINE-7-SULPHONIC ACID,
(F ACID.)

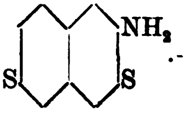
Fifty kilos. of 2-naphthol-7-sulphonic acid are heated with 100 kilos. of ammonia (22 per cent.) for six hours in an autoclave at 250°, or 33 kilos. of sodium naphthalene-2 : 7-disulphonate are heated with 25 kilos. of sodium hydroxide solution (40 per cent.) for ten hours at 200–250°, then 7 kilos. of ammonium chloride and 20 litres of water are added, and the temperature is kept at 200–250° for a further ten hours. In either case the product is dissolved in boiling water and the solution acidified, when, on cooling, the naphthylamine acid separates out (Cassella & Co., E.P., 12908 of 1886 ; F.P., 178978 ; G.P., 43740 ; U.S.P., 362560). A better method is to heat the sodium salt of the naphthol acid with 40 per cent. ammonium hydrogen sulphite solution and 20 per cent. ammonia at 100–150° (see under β-Naphthylamine, p. 187), the product being afterwards acidified.

The acid crystallises with $1H_2O$ and dissolves in 350 parts of boiling water. When boiled with a quantity of water insufficient to dissolve it, the crystalline acid changes into a very sparingly soluble, anhydrous powder.

The sodium salt crystallises with $4H_2O$ and dissolves in 70 parts of cold water. It also dissolves in hot, 90 per cent. alcohol.

The acid is used for making Diamine red 3B (Deltapurpurine 7B) and Rosazurine.

2-NAPHTHYLAMINE-3 : 6-DISULPHONIC ACID,

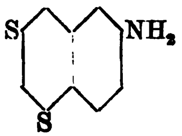


This is obtained by heating sodium 2-naphthol-3 : 6-disulphonate with ammonia in an autoclave at 200–250° (for methods see under 2-Naphthylamine-6-sulphonic acid, p. 206). The best process consists in heating the sodium salt with 40 per cent. ammonium hydrogen sulphite solution and 20 per cent. ammonia at 100–150° (see under β-Naphthylamine, p. 187), the product being afterwards acidified.

It is also formed by boiling 2-naphthylamine-3 : 6 : 8-trisulphonic acid with zinc dust and sodium hydroxide solution (see p. 196).

It is used for making Salmon red, Pyramine orange 2R, Congo orange G and R, Brilliant Congo G and R, Benzo fast red 9BL, Dianol brilliant red extra (Diphenyl red 8G), Trypan red, and Brilliant purpurine R.

2-NAPHTHYLAMINE-5 : 7-DISULPHONIC ACID,



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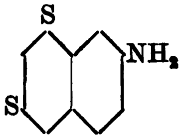
2-Naphthylamine-5-sulphonic acid (p. 205) is stirred into four times its weight of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide) at a temperature not exceeding 20° and the mixture kept at that point for one hundred and sixteen to one hundred and twenty hours. The product is neutralised with milk of lime, the gypsum filtered off and the calcium salts in the filtrate are converted into potassium salts. On concentration, the dipotassium salt of 2-naphthylamine-1 : 5-disulphonic acid separates out, whilst the acid potassium salt of the 5 : 7-disulphonic acid is obtained as chief product by acidifying the filtrate (Armstrong and Wynne, *Proc.*, 1890, 6, 129).

The acid is also produced by the sulphonation of β-naphthylamine (see p. 209) or of 2-naphthylamine-7-sulphonic acid. Twenty kilos. of the latter are added to 80 kilos. of cold fuming sulphuric acid (containing 20–30 per cent. of sulphur trioxide) and stirred for two days at the ordinary temperature. The mass is then poured into water, neutralised with milk of lime, the gypsum filtered off, and the calcium salts are converted into potassium salts, the solution of which is evaporated to 60 litres. After one or two days the potassium salt of 2-naphthylamine-1 : 7-disulphonic acid separates and can be purified by recrystallisation from hot water. The filtrate is heated and acidified with hydrochloric acid, when, on cooling, the acid potassium salts separate out. These are filtered off, dissolved in a little boiling water, and converted into the acid barium salts by adding a hot saturated solution of 11 kilos. of barium chloride ; on cooling, the barium salts are filtered off. They are then converted by sodium carbonate solution into the neutral sodium salts and, after the barium carbonate has been filtered off, the solution is evaporated to about 25 litres. After some days, a precipitate of the neutral sodium salt of 2-naphthylamine-4 : 7-disulphonic acid has formed, which is removed by a vacuum filter or centrifuge and can be purified by recrystallisation from water. The filtrate, containing the 2-naphthylamine-5 : 7-disulphonic acid, is acidified hot, when, on cooling, the acid sodium salt separates out. The yield of the latter is about 50 per cent. and that of each of the two other acids about 25 per cent. (Farbenfabriken vorm. F. Bayer & Co., G.P., 79243).

It is used for making 2-amino-5-naphthol-7-sulphonic acid (J acid).

2-Naphthylamine-6 : 8-disulphonic Acid,



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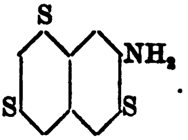
This is obtained by heating sodium or potassium 2-naphthol-6 : 8-disulphonate (G salt) with ammonia in an autoclave to a pressure of 40 atmospheres, or, better, with concentrated sodium bisulphite solution (0·3 part) and 20 per cent. ammonia (0·6 part) at 180° for six hours (see under β-Naphthylamine, p. 187), the product being afterwards acidified.

Another process (Gans & Co., E.P., 814 of 1884 ; G.P., 35019), in which also 2-naphthylamine-5 : 7-disulphonic acid is produced, is to add 10 kilos. of β-naphthylamine sulphate to 30 kilos. of fuming sulphuric acid (containing 20–30 per cent. of sulphur trioxide) and to heat the mixture to 110–140° until a sample gives a clear solution with water. The product is poured into 200 litres of water, neutralised with lime, the gypsum filtered off, and the calcium salt converted into sodium or potassium salt. It seems probable that the acid is isolated as its acid potassium salt.

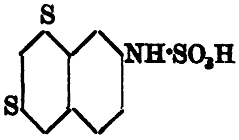
The acid and salts are readily soluble.

It is used for making 2-amino-8-naphthol-6-sulphonic acid (γ-acid), Crumpsall yellow, Brilliant croceine 9B, Diamine blue 6G, and Naphthol black B (Wool black B, Brilliant black B).

2-NAPHTHYLAMINE-3 : 6 : 8-TRISULPHONIC ACID,



The acid potassium salt of 2-naphthylamine-6 : 8-disulphonic acid is added to four parts of fuming sulphuric acid (containing 40 per cent. of sulphur trioxide) and the mixture heated slowly to 80–90°. It is kept at this temperature for ten to fifteen hours and then the temperature is raised to 120–130° and maintained at this point until the contents can be diazotised (in the first stage of the reaction the sulphamic acid,

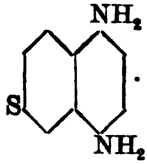


is formed, which cannot be diazotised), or until a sample, rendered alkaline, is no longer yellow. The mass is then poured into water, neutralised with milk of lime, the gypsum filtered off, and the calcium salt converted into potassium salt; the solution, on evaporation and acidification, furnishes the acid potassium salt of the trisulphonic acid (Dressel and Kothe, *Ber.*, 1894, **27**, 2153).

The acid potassium salt crystallises with $1\frac{1}{2}H_2O$ and dissolves in 40 parts of water at 20°. The acid sodium salt is readily soluble.

It is used for making 2-amino-8-naphthol-3 : 6-disulphonic acid.

1 : 4-NAPHTHYLENEDIAMINE-6-SULPHONIC ACID,



This acid is generally prepared in the form of its monoacetyl compound, which is diazotised and combined with a component, and then the acetyl group is eliminated and the free amino-group diazotised and combined with a second component.

The acetyl compound can be obtained by adding monoacetyl-1 : 4-naphthylenediamine sulphate (25 kilos.) to fuming sulphuric acid containing 20 per cent. of sulphur trioxide (75 kilos.) at 20°, and, when all is dissolved, warming for about an hour to 40–50°. The mass is poured into about 1,000 litres of water and 200 kilos. of ice, neutralised with slaked lime, and the filtered solution, after conversion into the sodium salt, used direct for making azo-dyes, or the solution is hydrolysed by boiling with dilute sulphuric acid, whereby the free acid separates out (Dahl & Co., G.P., 66354).

A more convenient method is to acetylate a mixture of 1-naphthylamine-6- and -7-sulphonic acids (Cleve's acids) with glacial acetic acid, and, after distilling off the excess of acetic acid, to dissolve 265 kilos. of the product in 1,300 kilos. of sulphuric acid and add 160 kilos. of a mixture of nitric and sulphuric acids containing 43 per cent. of nitric acid, the mixture being cooled. After a short time the nitration mixture is diluted with ice and water to 3,000 litres and the sodium salts of the nitro-acids are precipitated by adding 500 kilos. of salt. For the reduction, 31 kilos. of the mixture of nitro-acids are gradually added to a boiling mixture of 50 kilos. of iron borings, 100 litres of water, and 3 kilos. of 50 per cent. acetic acid. When the liquid is decolorised, sodium carbonate is added to precipitate the iron, the whole is filtered, and the acetyl derivative precipitated by the addition of 20 kilos. of hydrochloric acid (Cassella & Co., E.P., 15444 of 1893; F.P., 232299; G.P., 74177).

A further process is the following: 9·3 kilos. of aniline are diazotised and combined with 24·5 kilos. of the mixed sodium salts of 1-naphthylamine-6- and -7-sulphonic acids (Cleve's acids). The dye is collected in a filter press, mixed with water to a thin paste, and reduced with 30 kilos. of iron borings and 2 litres of acetic acid (30 per cent.). The reduction product is rendered alkaline with sodium carbonate, filtered hot, and the filtrate faintly acidified, care being taken to avoid an excess of mineral acid, when the 1 : 4-naphthylenediamine-6-sulphonic acid is precipitated (Levinstein, E.P., 12119 of 1898 ; U.S.P., 700574). It is then acetylated as follows :

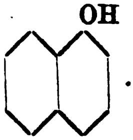
A mixture of 50 kilos. of the acid, 50 kilos. of 65–70 per cent. acetic acid, and 28–30 kilos. of crystallised sodium acetate is boiled under a reflux condenser for twenty to twenty-five hours. When a sample is soluble in water and, after acidifying, can be diazotised without the evolution of nitrogen, the acetylation is finished, and the mass can be dissolved in water and used direct for making dyes (Cassella & Co., F.P., 284591 ; G.P., 116922).

Alternatively, the azo-dye from diazotised aniline and Cleve's acids can be acetylated by boiling it with glacial acetic acid and acetic anhydride and the acetylated dye reduced with iron and acetic acid as above, giving the acetyl compound of 1 : 4-naphthylenediamine-6-sulphonic acid (Levinstein, *loc. cit.*). The former process is, however, to be preferred.

The acid is very sparingly soluble, as is also the acetyl derivative. It is used (in the form of its acetyl compound) for making the Diaminogen blues.

Naphthols and their Sulphonic Acids.

α-Naphthol,



The fusion of sodium naphthalene-α-sulphonate with sodium hydroxide is carried out precisely as in the case of the manufacture of β-naphthol, the limits of temperature being 270–320°.

α-Naphthol can also be prepared by hydrolysing α-naphthylamine salts, thus 40 kilos. of α-naphthylamine sulphate or hydrochloride and 200 litres of water are heated in an autoclave for four hours at 200°. On cooling, the α-naphthol is collected and distilled in a vacuum. The ammonia is recovered from the aqueous liquid by distillation with lime (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 14301 of 1892 ; F.P., 223550 ; G.P., 74879). Alternatively, α-naphthylamine may be heated with sodium hydrogen sulphate, phosphoric acid, or zinc chloride and water at 210° (Farbwerke vorm. Meister, Lucius, & Brüning, G.P., 76595).

α-Naphthol melts at 94°, boils at 278–280°, and has D^4 1·224. It is only sparingly soluble in hot water, although more readily so than β-naphthol, and is readily volatile with steam.

α-Naphthol is used chiefly for the manufacture of Naphthol Yellow S.

β-Naphthol,*

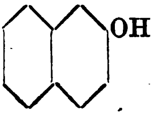


Fig. 23 shows the arrangement of a plant for the manufacture of β-naphthol; the production of sodium naphthalene-β-sulphonate is described on p. 173.

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* Full details of the fusion process are given under Phenol, p. 104.

One hundred kilos. of sodium hydroxide are melted with 20 litres of water and at 200° 160 kilos. of sodium naphthalene-β-sulphonate are gradually added. The temperature is raised to 280–300° and the fusion is complete in five to six hours. The liquid mass is then run into 2,000 litres of water and hydrochloric acid (about 100 kilos.) added to liberate the naphthol, but not sufficient to decompose the sodium sulphite. The β-naphthol is filtered in a filter press and purified by distillation in a vacuum.

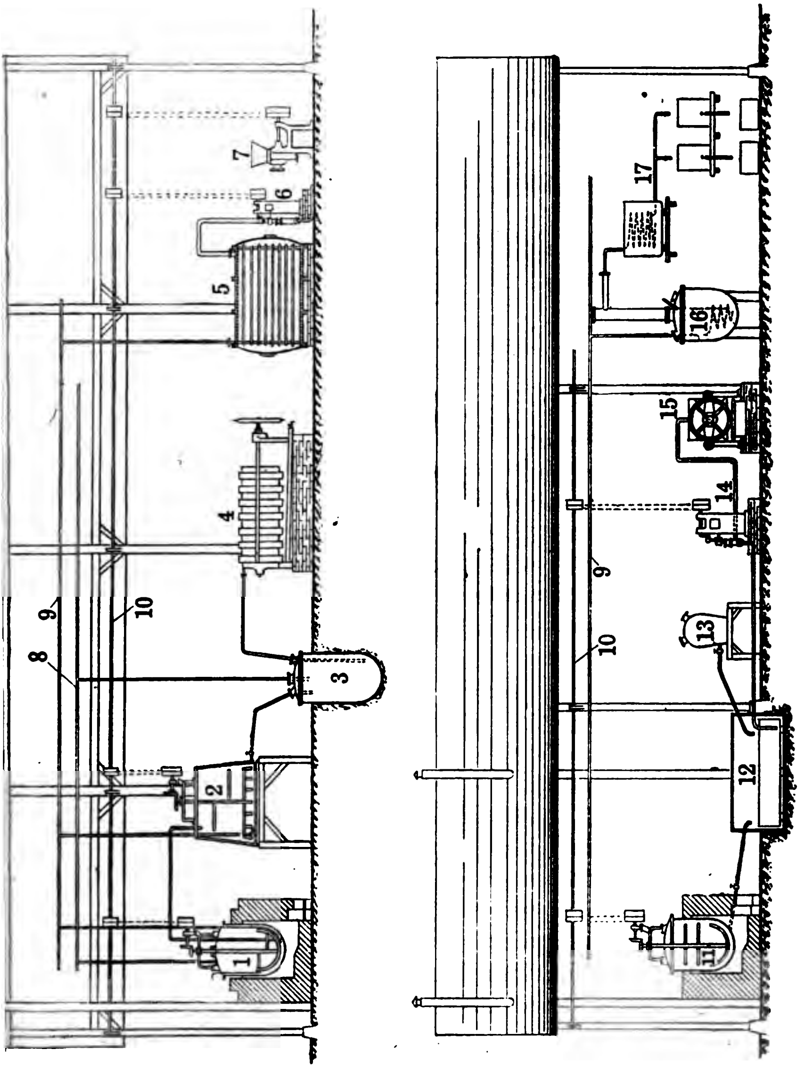


FIG. 23.—PLANT FOR THE MANUFACTURE OF β-NAPHTHOL.

1, Sulphonation pan; 2, tub for precipitating sodium naphthalene-β-sulphonate; 3, egg; 4, filter press; 5, vacuum drying stove; 6, vacuum pump; 7, mill for grinding the dry product; 8 compressed-air pipe; 9, steam-pipe; 10, shafting; 11, melt-pan; 12, vessel for precipitating β-naphthol; 13, hydrochloric acid reservoir; 14, pump; 15, filter press for naphthol; 16, vacuum still; 17, condenser and receivers for distillate.

Fig. 24 shows a modern naphthol vacuum still. It consists of a cast iron pan with a bolted-on cover, in which is a large manhole. The pan is set in brickwork, and can be heated either by direct fire or by gas. The material to be distilled must be perfectly dry. The lid carries a short fractionating column, and the vapours pass through this to a jacketed condenser, the outside of which is sprayed with water. The ends of this condenser are fitted with sight-glasses through which the course of the distillation is observed and any stoppage detected. The lower end of the condenser is fitted with a tap by means of which the distillate can be directed to either of the two receivers. It is necessary to separate the first runnings from the main distillate, and the former are therefore collected in the small receiver and the pure product is then diverted through a horizontal cylinder where the vapours are freed from accompanying impurities, into the principal receiver. In the distillation process, about 10–15 per cent. of the weight of naphthol remains behind as tar. The yield is 80 kilos. (Grandmougin, *Rev. prod. Chim.*, 1917, **20**, 197).

In carrying out the fusion in an open pan, a certain amount of oxidation takes place and it is an advantage to use a pan which can be closed when the mass begins to swell up. Indeed, recent laboratory experiments have shown that the yield is increased by effecting the fusion in an atmosphere free from oxygen (Boswell and Dickson, *J. Amer. Chem. Soc.*, 1918, **40**, 1786).

β-Naphthol of a high degree of purity is said to be obtained by heating in an autoclave 46 parts of sodium naphthalene-β-sulphonate with 50 parts of sodium hydroxide (40° Bé.) for ten to twenty hours at 300–330°. The β-naphthol, after cooling, is separated as described above (Aktiengesellschaft für Anilinfabrikation, F.P., 469040). Willson and Meyer (*Ber.*, 1914, **47**, 3160) employ 10 per cent. sodium hydroxide at 300°.

As it is difficult to prepare sodium naphthalene-β-sulphonate free from the α-compound, the crude β-naphthol usually contains some α-naphthol which is not removed by vacuum distillation. The naphthoxide solution is therefore treated with acid sufficient only to liberate about 85 per cent. of the naphthol, which is filtered off when cold. This consists of the pure product. The filtrate is strongly diluted with the wash-water from the molten naphthol (before being distilled) and then acidified, when the rest of the β-naphthol is precipitated, the α-compound remaining in solution.

β-Naphthol melts at 122°, boils at 285–286°, and has D^4 1·217.

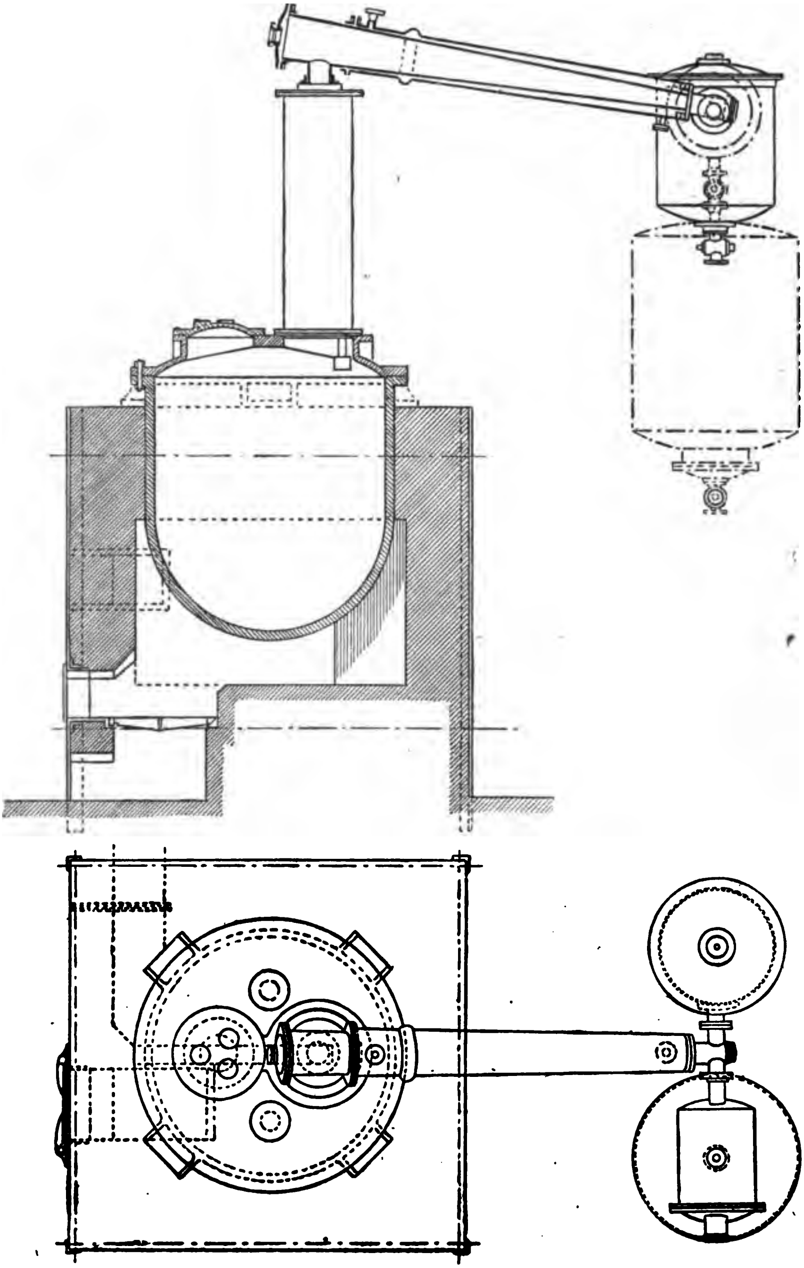
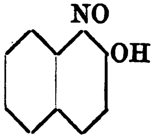


FIG. 24.

It sublimes easily and can be distilled in a current of superheated steam. It is sparingly soluble in water, its solubility being less than that of α-naphthol.

β-Naphthol is used for making naphtholsulphonic acids, for the production of Para-red and other dyes on the fibre, for making nitroso-β-naphthol, and Oil Yellow (Sudan I), Pigment orange R, Tannin orange R, Sudan II, III and IV, Azarine S, Pigment purple A, Tuscaline orange G, Sudan brown, Autol red, Indoin blue, Permanent orange R, Lake red C, D and P, Orange II, Fast orange O, Orange R, Palatine chrome violet, Acid alizarine black R, Fast red A, Brilliant fast red G, Palatine chrome black 6B (Salicine black U, UL), Eriochrome black A, Cloth scarlet G and R, Double scarlet, Eriochrome verdone A, Granite black, Fast sulphone black F and FB, Diamine blue 6G, Trisulphone violet B, Trisulphone blue B and R, Acid anthracene red 3B, Chicago blue RW, Coomassie navy blue, Meldola's blue and New blue R.

α-NITROSO-β-NAPHTHOL,



The following process can easily be adapted to the large scale.

Fifty grams of β-naphthol are dissolved in 14 grams of sodium hydroxide and 500 c.c. of water, the solution is diluted with 1 litre of water, and 25 grams of sodium nitrite are added. The solution is cooled by the addition of about 500 grams of ice, and 700 c.c. of 10 per cent. sulphuric acid are stirred in gradually, the temperature being kept at about 5°. The nitrosonaphthol soon separates as a pale greenish-yellow precipitate, which is filtered off after about two to three hours, and washed with water until the washwater is only faintly acid (Lagodzinski and Hardine, *Ber.*, 1894, **27**, 3075).

Care must be taken that no metal comes into contact with the substance.

α-Nitroso-β-naphthol melts at 112° and is sparingly soluble in water, but readily so in the ordinary organic solvents.

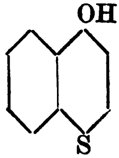
It is used for making 1-amino-2-naphthol-4-sulphonic acid, and also comes on the market as Gambine Y (Fast printing green).

α-NAPHTHOLSULPHONIC ACIDS.

By sulphonating α-naphthol, a mixture of the 1 : 2- and 1 : 4-naphtholsulphonic acids is obtained which on further sulphonation gives 1-naphthol-2 : 4-disulphonic acid. This yields 1-naphthol-2 : 4 : 7-trisulphonic acid, which, on partial hydrolysis, gives the 2 : 7- and 4 : 7-disulphonic acids and the 7-sulphonic acid.

The technically important α-naphtholsulphonic acids are prepared (1) from the corresponding α-naphthylaminesulphonic acids either by the diazo-reaction or by the bisulphite reaction, or (2) from the corresponding sulphonic acids by fusion with sodium hydroxide.

1-Naphthol-4-sulphonic Acid,
(Nevile and Winther's Acid)



(1) One hundred kilos. of sodium naphthionate and 100 kilos. of 50 per cent. sodium hydroxide solution are heated in an autoclave for eight to ten hours at 240–260°. On cooling, the mass is dissolved in 750 litres of hot water, the ammonia boiled off, and the solution neutralised with hydrochloric acid. It can be used directly for making azo-dyes, or the NW acid can be precipitated as sodium salt by adding sodium chloride (Aktiengesellschaft für Anilinfabrikation, G.P., 46307).

(2) Forty-five kilos. of sodium naphthionate are dissolved in water, 80 kilos. of hydrochloric acid added, and the naphthionic acid is diazotised by a 25 per cent. solution of 37·5 kilos. of sodium nitrite. The diazo-compound is allowed to settle, the liquor drawn off, the precipitate washed twice with water, and made up to 450 litres. This mixture is then run gradually into a boiling mixture of 750 kilos. of water and 37·5 kilos. of sulphuric acid. Nitrogen is evolved, and the solution turns red owing to the combination of some of the diazo-compound with the NW acid. When gas ceases to be evolved, the solution is neutralised with 46 kilos. of sodium carbonate and used direct for making azo-dyes. The yield of NW acid is about 80 per cent. of the theoretical (Nevile and Winther, *Trans.*, 1880, 37, 632 ; Dahl, E.P., 2296 of 1883 ; Erdmann, *Annalen*, 1888, 247, 341).

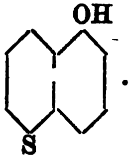
(3) Thirty-two kilos. of sodium naphthionate, 20 litres of water, and 75 kilos. of sodium hydrogen sulphite (40° Bé.) are heated in an open enamelled pan for twenty-four hours at 85–90°. The product is acidified with hydrochloric acid, any precipitated naphthionic acid is filtered off, the filtrate is rendered alkaline with sodium hydroxide, boiled to expel ammonia, then acidified with hydrochloric acid, boiled to expel sulphur dioxide, and the

solution used direct, or salt added to precipitate the sodium salt of NW acid (Farbenfabriken vorm. F. Bayer & Co., E.P., 16807 of 1899; F.P., 292882; G.P., 109102). This method of preparation gives the best results.

The acid and salts are readily soluble in water, but the sodium salt can easily be salted out of solution.

The acid is used for making a large number of azo-dyes, among which are Double scarlet R, Azoeosine (Buffalo Flamine G), Azorubine, Double scarlet extra S, Rosophenine pink, Cloth red B and G, Diamond black, Violet black, Azo blue, Oxamine blue 4R, Diamine blue BX, Benzoazurine G, and Benzo black blue.

1-NAPHTHOL-5-SULPHONIC ACID, (L ACID)



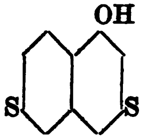
Preparation from Naphthalene-1 : *5-disulphonic Acid.*—One hundred kilos. of sodium naphthalene-1 : 5-disulphonate are heated with 300–400 kilos. of sodium hydroxide in a cast iron pan with stirrer to 160–190°. The mass is then dissolved in 1,500 litres of water, just acidified with hydrochloric acid, and filtered. On cooling, the sodium salt of 1-naphthol-5-sulphonic acid separates completely (Ewer and Pick, G.P., 41934).

Preparation from 1-*Naphthylamine-5-sulphonic Acid.*—The acid is diazotised and the diazo-compound decomposed by boiling dilute sulphuric acid as in the preparation of 1-naphthol-4-sulphonic acid (p. 217) (Verein Chemischer Fabriken, E.P., 2237 of 1883; G.P., 26012; Schoellkopf Aniline and Chemical Co., E.P., 15781 of 1885; F.P., 173084; G.P., 40571; U.S.P., 333034).

The acid and its salts are readily soluble in water.

It is used for making Cochineal scarlet 4R, Double ponceau, Fast red VR, Diamond black, Benzoazurine 3G, and Milling scarlet B and 6B.

1-NAPHTHOL-3 : 6-DISULPHONIC ACID,



Preparation from Naphthalene-1 : 3 : *6-trisulphonic Acid.*—One part of sodium naphthalene-1 : 3 : 6-trisulphonate is heated with half a part of sodium hydroxide and half a part of water to

170–180° for several hours in an autoclave (Gürke and Rudolph, E.P., 15716 of 1885; G.P., 38281).

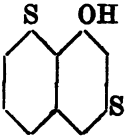
Preparation from 1-*Naphthylamine*-3 : 6-*disulphonic Acid.*—The acid is diazotised in the usual way and the diazo-solution decomposed by adding it to boiling dilute sulphuric acid (compare p. 217) (Freund, E.P., 1069 of 1883; F.P., 153847; G.P., 27346).

Another method consists in heating the acid with 3 parts of water at 180° (Cassella & Co., G.P. Anm. C., 4375).

The acid sodium salt dissolves readily in water.

It is used for making Lanafuchsines (Sorbine reds), Palatine scarlet A, Palatine red A, Azo red A, and Croceine AZ.

1-NAPHTHOL-3 : 8-DISULPHONIC ACID,
(ε-ACID)



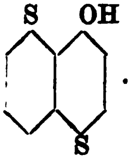
Preparation from 1-*Naphthylamine*-3 : 8-*disulphonic Acid.*—The acid sodium salt of 1-naphthylamine-3 : 8-disulphonic acid (equivalent to 100 kilos. of 100 per cent.) is converted into the corresponding naphthol acid exactly as in the case of the preparation of 1-naphthol-4 : 8-disulphonic acid (below). Here, however, no sultone separates after decomposing the diazo-solution. After liming, etc., 2,900–3,000 litres of a 2–3 per cent. solution of sodium 1-naphthol-3 : 8-disulphonate are obtained, which can be used directly for making azo-dyes.

An alternative method is to heat 10 kilos. of the acid sodium salt of 1-naphthylamine-3 : 8-disulphonic acid with 40 kilos. of water for five to eight hours in an autoclave at 180°. The 1-naphthol-3 : 8-disulphonic acid is obtained from the solution by salting out or evaporating (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 14301 of 1892; F.P., 223550; G.P., 71494).

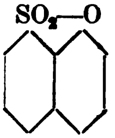
The disodium salt crystallises with $6H_2O$ and dissolves in about 5·5 parts of cold water.

It is used for making Eosamines, Erica 2GN and B, Columbia blue G and R, and Benzo fast blue B and R.

1-NAPHTHOL-4 : 8-DISULPHONIC ACID,
(S *or* δ ACID)



Preparation from 1-*Naphthylamine*-4 : 8-*disulphonic Acid.*—Two hundred kilos. of the recrystallised acid sodium salt of the amino-acid (p. 200) or an amount equal to 100 kilos. of the pure salt are dissolved in 1,000 litres of water with the addition of 15 kilos. of sodium carbonate and the solution is cooled to 5–10° by adding ice. This temperature is maintained while 75 kilos. of concentrated sulphuric acid are run in slowly, the whole being well stirred. The amino-acid separates out and is diazotised by running in 18–20 kilos. of sodium nitrite dissolved in 150 kilos. of water. The end of the diazotisation is shown by testing with starch-iodide paper. The volume of the diazo-solution will be about 1,500 litres. It is now run in a thin stream into a boiling mixture of 250 kilos. of water and 15 kilos. of concentrated sulphuric acid. The solution foams with the evolved nitrogen, and when all the diazo-solution has been added the whole is boiled for half an hour to complete the decomposition. The volume is now 2,200 litres. The solution is allowed to cool, when a little of the decomposition product of admixed 1-naphthylamine-8-sulphonic acid (see p. 200), namely, the sultone



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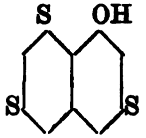
separates. This is filtered off, and is converted into the 1-naphthol-4 : 8-disulphonic acid by sulphonation with 3–5 parts of sulphuric acid (66° Bé.). The filtrate from the sultone is neutralised with slaked lime, the gypsum filtered off, the solution of calcium salt treated with sodium carbonate to obtain the sodium salt and filtered. This solution can be used directly for making azo-dyes, but is evaporated to dryness, or partly evaporated, and then salted out, if the dry acid is required (Paul, *Zeitsch. angew. Chem.*, 1896, **9**, 559).

The acid is also obtained by treating 1 : 8-naphthasultone (from 1-naphthol-8-sulphonic acid) with 2–3 parts of sulphuric acid for one hour at 80–90° until the product is soluble in water (Schoellkopf Aniline & Chemical Co., E.P., 15775 of 1885 ; F.P., 173083 ; G.P., 40571 ; U.S.P., 333034 ; Badische Anilin- & Soda-Fabrik, addition to F.P., 200023 ; G.P., 57388).

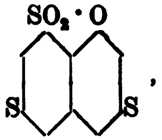
The disodium salt crystallises with $1H_2O$ and is readily soluble in water.

It is used for making Azocochineal, Geranine 2B, and Croceine B.

1-NAPHTHOL-3 : 6 : 8-TRISULPHONIC ACID,



This is prepared from 1-naphthylamine-3 : 6 : 8-trisulphonic acid (p. 202) by adding a large excess of sulphuric acid to a solution of the disodium salt, diazotising with the requisite amount of sodium nitrite, and boiling until the evolution of nitrogen has ceased. The solution is neutralised with milk of lime, filtered, and the calcium salt converted into the sodium salt. If the solution is not treated with lime, the disodium salt of the naphthasultonedisulphonic acid,



crystallises out on cooling (Koch, E.P., 9258 of 1890; G.P., 56058). Another process is to heat 10 kilos. of the disodium salt with 40 kilos. of water for five to ten hours in an autoclave at 180–250°. The naphtholtrisulphonic acid is obtained by salting it out of solution or by evaporation (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 14301 of 1892; F.P., 223550; G.P., 71495).

The acid is used for making chromotrope acid, Trisulphone violet B, and Trisulphone blue R and B.

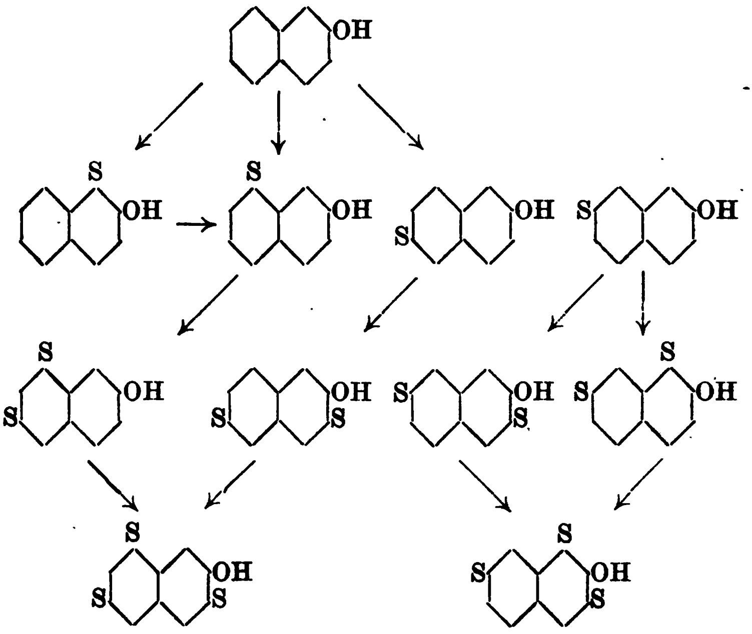
β-NAPHTHOLSULPHONIC ACIDS.

The first product of the action of sulphuric acid on β-naphthol is the 1-sulphonic acid. With more sulphuric acid or at a higher temperature, a mixture of the 8- and 6-sulphonic acids is obtained. The highest proportion of the 8-sulphonic acid is formed at a fairly low temperature, whilst the 6-sulphonic acid is produced on heating further. Sulphonation to the disulphonic stage gives, in addition to some of the 6-sulphonic acid, the 6 : 8- and the 3 : 6-disulphonic acids, the former being produced from the 8- and the latter from the 6-sulphonic acid. The 8-mono- and the 6 : 8-disulphonic acids correspond in certain properties; for example, their salts are more readily soluble in water, salt solution, or alcohol than those of the 6-mono- and 3 : 6-disulphonic acids which also correspond in properties. Further, the first pair of acids combine with diazo-compounds with much greater difficulty than the latter pair, and the azo-dyes produced from the 8-mono- and 6 : 8-disulphonic acids are much yellower than those from the 6-mono- and 3 : 6-disulphonic acids. For this reason, the 6 : 8-disulphonic acid is called " G acid " (gelb = yellow) and the 3 : 6-acid " R acid."

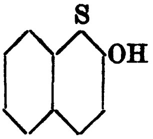
On further sulphonation, both the 6 : 8- and the 3 : 6-disulphonic acids yield the 3 : 6 : 8-trisulphonic acid.

The 7-monosulphonic acid is prepared by fusing naphthalene-2 : 7-disulphonic acid with sodium hydroxide. On sulphonation, it yields the 3 : 7-disulphonic acid or (with chlorosulphonic acid) the 1 : 7-disulphonic acid.

The following scheme shows these relationships.



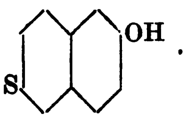
2-NAPHTHOL-1-SULPHONIC ACID,



This was first prepared by Stebbins (U.S.P., 256400) by treating β-naphthol with 3 parts of sulphuric acid at 20°, diluting with water, filtering from unchanged naphthol, neutralising with milk of lime, converting the calcium salts into sodium salts, and extracting the dry salts with 4 parts of 90 per cent. alcohol. The filtrate, on evaporation, gave the sodium salt of 2-naphthol-1-sulphonic acid. It is best obtained by Tobias's method (E.P., 15404 of 1893; F.P., 232467; G.P., 74688) by adding 1 part of β-naphthol to 2–2½ parts of sulphuric acid (90–92 per cent.). The temperature rises to about 40° and is kept at this point for ten minutes, when the mass solidifies. It is diluted with water, and the sodium salt is obtained by partial neutralisation with sodium carbonate or by salting out. A little of the 2-naphthol-8-sulphonic acid is left in the mother liquor. Alternatively, the calcium salt may be made, using calcium carbonate at the end of the neutralisation to avoid splitting off the sulphonic acid group, and the sparingly soluble basic barium salt precipitated from the solution. In preparing the calcium salt, a little β-naphthol separates, which can be filtered off, dried, and used over again. When treated with a diazo-compound, the sulphonic acid group is eliminated and an azo-derivative of β-naphthol formed. With the exception of the basic barium salt, the salts are readily soluble in water.

The acid is used for making 2-naphthylamine-1-sulphonic acid.

2-Naphthol-6-sulphonic Acid,
(Schaeffer Acid)

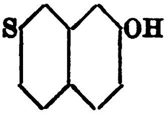


One hundred kilos. of β-naphthol are heated with 69 kilos. of sulphuric acid (100 per cent.) at 100° until sulphonation is practically complete. The mass is dissolved in hot water, the acids converted into acid salts by adding 38 kilos. of sodium carbonate, the solution filtered, if necessary, from any unattacked naphthol, and saturated with common salt. The Schaeffer salt is precipitated and is filtered off (Leipziger Anilinfabrik Beyer & Kegel, E.P., 7098 of 1884; G.P., 32964). The formation of Schaeffer acid in the manufacture of croceine acid and its separation therefrom is fully described on p. 225. The acid melts at 125° and is readily soluble in water or alcohol.

The sodium salt crystallises with $2H_2O$ and dissolves in about 3·3 parts of water at 80°, in 57·8 parts at 14°, and in 69 parts at 11·5°. The calcium salt crystallises with $5H_2O$ and dissolves in 30 parts of water at 18°.

Schaeffer's acid is used for making 2-naphthylamine-6-sulphonic acid and for Naphthol green B, Ponceau 4GB (Croceine orange), Brilliant orange O and R, Fast red BT, Clayton cloth scarlet, Pigment scarlet G, Bordeaux BX and G, Cloth red G, and Diaminogen blue BB.

2-NAPHTHOL-7-SULPHONIC ACID, (F ACID)



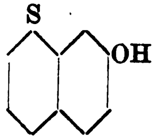
One hundred kilos. of sodium naphthalene-2 : 7-disulphonate are heated with 400 kilos. of sodium hydroxide solution (50 per cent.) in an autoclave at 225° for ten hours (compare p. 207) until an acidified sample, on extraction with ether, shows the presence of traces of dihydroxynaphthalene, or until a sample freed from sulphur dioxide gives with diazoxylene an amount of azo-dye equivalent to the amount of sodium salt employed. The melt is then dissolved in about 1,000 litres of water, acidified with hydrochloric acid, and the sulphur dioxide boiled off. The solution so obtained can be used directly for making azo-dyes or can be allowed to cool, whereby the sodium salt of F acid crystallises out (Cassella & Co., E.P., 12908 of 1886; F.P., 178978; G.P., 42112).

If the crude mixture of naphthalene-2 : 6- and -2 : 7-acids obtained in the sulphonation of naphthalene is treated with sodium hydroxide, a mixture of F acid and Schaeffer acid is obtained. For example, 130 kilos. of the mixed disulphonic acids are heated with 35 kilos. of sodium hydroxide, 180 litres of water, and 40 kilos. of sodium chloride in an autoclave for sixteen hours at 240–270°. On cooling, the crystals are separated from the mother liquor; they consist of sodium sulphite and the basic sodium salt of Schaeffer's acid; the alkaline mother liquor contains chiefly the basic sodium salt of F acid. It is acidified and the sodium naphthol-7-sulphonate salted out. Alternatively, the product of the melt can be dissolved in 500 litres of water, the sulphur dioxide expelled by hydrochloric acid, and the boiling liquid saturated with salt. After a little while the boiling solution is filtered. The sodium salt of Schaeffer's acid remains behind, whilst the sodium salt of F acid crystallises from the filtrate on cooling (Cassella & Co., G.P., 45221). For making Deltapurpurine 5B the two acids are not separated, but are heated with ammonia to give a mixture of the corresponding amino-acids, which is used direct.

The acid melts at 89° and is readily soluble in water. The sodium salt crystallises with $2\frac{1}{2}H_2O$ and dissolves in 12·5 parts of water at 15°.

The sodium salt is used for making 2-naphthylamine-7-sulphonic acid, and a mixture of it with β-naphthol, containing 10 per cent. of the former, known as Naphthol R, is used for producing paranitraniline red on the fibre.

2-NAPHTHOL-8-SULPHONIC ACID, (CROCEINE ACID)



One hundred kilos. of β-naphthol are stirred as quickly as possible into 200 kilos. of sulphuric acid or sulphuric acid mixed with a little fuming acid. The mixture becomes warm, and the temperature must not rise above 50–60°. When all is dissolved (ten to fifteen minutes) the mass is stirred into cold water. The neutral sodium salts are prepared in the usual way, dried, and boiled with 3–4 parts of alcohol (90 per cent.) and filtered hot. The sodium salt of Schaeffer's acid remains undissolved, whilst the sodium salt of croceine acid is contained in the solution and separates out on cooling (Farbenfabriken vorm. F. Bayer & Co., E.P., 1225 of 1881; F.P., 142024; G.P., 18027, 20397; U.S.P., 256381).

The separation of the two acids may also be effected by combining the Schaeffer salt with diazobenzene, diazotoluene, diazoxylene, or diazonaphthalene, which combine only very slowly with the croceine acid. The quantity of diazo-compound required is ascertained previously by tests made on a small portion. When the Schaeffer acid is all combined, the azo-dye is salted out by adding salt solution and is filtered off, the filtrate containing the croceine acid being used direct for making azo-dyes (Farbenfabriken vorm. F. Bayer & Co., E.P., 2411 of 1883; G.P., 26231). Tetrazotised benzidine, tolidine, etc., may also be used (*idem*, E.P., 8495 of 1884; G.P., 30077).

A further method by which nearly all the Schaeffer salt can be separated consists in (1) dissolving the sulphonation mixture in 10 parts of water, neutralising with milk of lime, filtering, and evaporating until the salt of the Schaeffer acid separates out; (2) dissolving the sulphonation mixture in 2 parts of water and neutralising with solid sodium carbonate, whereby the sodium salt of Schaeffer's acid separates out, or (3) dissolving the sulphonation mixture in 3 parts of water and adding about two-thirds of the quantity of sodium hydroxide necessary to neutralise the whole. On cooling, the sodium salt of Schaeffer's acid separates out. In each case about four-fifths of the Schaeffer acid present is separated. The filtrate of croceine acid, containing a small amount of Schaeffer acid, can be used direct for making azo-dyes, or, if necessary, can be freed from the last traces of Schaeffer acid by one of the methods described above (Farbenfabriken vorm. F. Bayer & Co., E.P., 8390 of 1884 ; G.P., 26673).

According to Leonhardt and Schulz (G.P., 33857), the acid is obtained by treating β-naphthol with 2 parts of sulphuric acid at 20° for about seven days. The 2-naphthol-1-sulphonic acid first formed is gradually converted into croceine acid, and very little Schaeffer acid is formed.

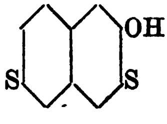
Another method of preparation consists in boiling 222 kilos. of 2-naphthylamine-8-sulphonic acid with 1,200 kilos. of sodium hydrogen sulphite (40° Bé.) until solution is effected. The solution is then treated with sodium hydroxide to expel ammonia, then acidified with hydrochloric acid, and boiled to remove sulphur dioxide. The solution may be neutralised with sodium carbonate and used direct, or the sodium salt may be obtained by salting out (Badische Anilin- & Soda-Fabrik, G.P., 134401).

The naphthylaminesulphonic acid, when diazotised and the solution boiled with dilute sulphuric acid as described on pp. 217 and 219, also yields the naphthol acid (Dahl, E.P., 7712 of 1884 ; G.P., 29084).

The acid decomposes into β-naphthol and sulphuric acid when its solution is evaporated. The sodium salt is readily soluble in water.

It is used for making Croceine scarlet 3BX, 3B, O extra, and 8B, Congo rubine (Direct crimson B), Bordeaux COV, Heliotrope 2B, and Chicago blue 2R and 4R (Benzo blue 2R and 4R).

2-Naphthol-3 : 6-disulphonic Acid,
(R Acid)



Ten kilos. of β-naphthol are heated with 30 kilos. of sulphuric acid for twelve hours at 100–110°. The disulphonic acids are converted through the calcium salts into their sodium salts and the dry mixture is digested with 3–4 parts of alcohol (75-85 per cent. by weight). The R salt remains undissolved, whilst the filtrate contains the G salt, and is evaporated (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 1715 of 1878 ; F.P., 124811 ; G.P., 3229).

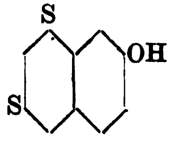
A later process (Leipziger Anilinfabrik Beyer & Kegel, E.P., 7097 of 1884 ; F.P., 161840 ; G.P., 33916 ; U.S.P., 351056) consists in adding 100 kilos. of β-naphthol quickly to 400 kilos. of sulphuric acid at 125° and maintaining the temperature at 125–150° for five to six hours. The mass is dissolved in hot water, neutralised with sodium carbonate, saturated with common salt, and allowed to cool, when the R salt separates out, the G salt remaining in solution. (One hundred c.c. of 20 per cent. salt solution dissolve 2·75 grams of R salt and 14·5 grams of G salt.) The R salt is filtered off and washed with saturated salt solution, both solid and filtrate being used direct for making azo-dyes. Equally good results are obtained by salting out the calcium salts.

Probably the best method of sulphonation is to add β-naphthol to 4–5 parts of sulphuric acid heated to 100° and to keep the mixture at 120° until a sample, when treated with excess of sodium nitrite, no longer shows the characteristic reaction of Schaeffer salt (intense eosine-red). A proposal by Baum (E.P., 3523 of 1883; G.P. Anm. B., 4199) to add equal weights of Schaeffer salt and potassium pyrosulphate to 2 parts of sulphuric acid at 120–130° and to heat at 150–160° for five to six hours offers no advantage. The separation of R salt from G salt and Schaeffer salt is also described on p. 228.

The acid is readily soluble in water, and the sodium salt also dissolves readily, but is sparingly soluble in salt solution or alcohol.

It is used for making 2-naphthylamine-3 : 6-disulphonic acid and for Ponceau G, R, 3R and 4R, Azogrenadine L, Archelline 2B (Bordeaux B, Fast red B), Amaranth, Acid alizarine red B (Palatine chrome red B), Cloth red B, Union Fast claret, Coomassie wool black S, Naphthol black B and 6B, etc.

2-Naphthol-6 : 8-disulphonic Acid, (G Acid)



A mixture consisting chiefly of G acid with some Schaeffer acid is obtained by adding 1 part of β-naphthol to 5 parts of sulphuric acid cooled to 0° and raising the temperature gradually to 60° in the course of thirty-six hours, or 1 part of β-naphthol is added to 4 parts of sulphuric acid, the temperature being allowed to rise to 50–60°. The mass is kept at 60° for forty-eight hours or at 20° for eight to ten days. The separation of the two acids can be effected by making use of the different solubilities of their barium, sodium, or potassium salts. The barium and sodium salts of Schaeffer acid are more insoluble than those of G acid, whilst the reverse holds good in the case of the potassium salts.

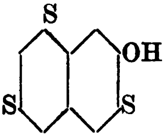
When the G acid is to be used for making azo-dyes, it is convenient to separate the Schaeffer salt by combining it with diazobenzene, etc. The solution of the sodium salts is titrated with diazotised α-naphthylamine, which does not immediately combine with G salt, and then the calculated amount of diazobenzene or other diazo-compound is run into the alkaline solution, the azo-dye salted out, filtered off, and the solution of pure G salt used direct (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 816 of 1884; G.P., 36491; Cassella & Co., U.S.P., 331059).

Another process consists in heating 750 parts of β-naphthol with 2,250 parts of sulphuric acid within one hour to 58–59° and to keep the mixture at this temperature for eight hours; it is then raised to 95° and kept at this point for four hours, after which the sulphonation is poured into 3,600 parts of water. The solution is added to a mixture of slaked lime, prepared from 930 parts of quicklime, and a concentrated solution of 812 parts of anhydrous sodium sulphate, which has been boiled. The mixture is neutralised with calcium carbonate, boiled, and filtered. The amount of R salt and Schaeffer salt in the filtrate is now determined by means of diazotised α-naphthylamine, and one-third of this weight of quicklime is slaked and added to the hot solution (thus, if the quantity of R and Schaeffer salt is found to be 540 parts, the amount of quicklime required is 180 parts). The precipitate, which contains the R salt, is mixed with 300–400 parts of boiling water, neutralised with sulphuric acid (about 150 parts), and filtered. The filtrate is heated to 80°, neutralised, if necessary, with a little hydrochloric acid, and salt added to make a 12 per cent. solution. The precipitate is filtered at 35° and consists of R salt. The filtrate, containing the Schaeffer and G salts, is treated with 50 parts of sodium carbonate, neutralised with hydrochloric acid, and evaporated to 28° Bé., the solution being kept neutral. It is cooled to 25° and filtered from the Schaeffer salt which separates out. (This is purified by mixing it with warm water, filtering, and washing with cold water.) The filtrate is heated to 95° and 1,200 parts of potassium chloride are added to precipitate the G salt which is filtered off when cold.

The salts of G acid, with the exception of the potassium salt which dissolves in 2·5 parts of boiling water, are easily soluble in water.

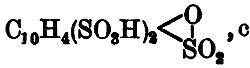
It is used for making β-naphthylamine-6 : 8-disulphonic acid and for Crystal ponceau, Erika G extra, Cochineal red A (Brilliant scarlet), Brilliant croceine 3B, and Diamine scarlet B.

2-NAPHTHOL-3 : 6 : 8-TRISULPHONIC ACID,



One part of β-naphthol is added to 4–5 parts of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide) sufficiently rapidly to cause the temperature to rise to 140–160°, and the mixture is kept at this temperature until a sample gives with ammonia a solution having a pure green fluorescence or, with diazoxylene in alkaline solution, an azo-dye only after some time. The mass is then neutralised with milk of lime and the calcium salt converted into the sodium salt in the usual manner (Meldola, E.P., 1864 of 1879 ; Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 2544 of 1882 ; F.P., 137109 ; G.P., 22038 ; U.S.P., 280317 ; compare also Endemann, U.S.P., 277864).

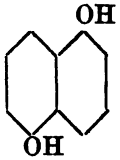
The same result is more conveniently attained by employing fuming sulphuric acid containing 40 per cent. of sulphur trioxide at 120° (Nietzki, *Chem. Zeit.*, 1891, **15**, 296) or 400 lb. of β-naphthol may be stirred into 1,200 lb. of sulphuric acid (100 per cent.), 1,180 lb. of fuming sulphuric acid (containing 40 per cent. of sulphur trioxide) added, the mixture heated to 125° and kept at that point for 1½–2 hours. It is then blown on 2,000 lb. of ice, 6,000 lb. of salt solution (24° Bé.) are added and the precipitated acid sodium salt is filtered off and washed with salt solution. Either of the acids 6- or 8-sulphonic, or 3 : 6- or 6 : 8-disulphonic, may be used instead of β-naphthol (Levinstein, E.P., 706 of 1883 ; *Ber.*, 1883, **16**, 462 ; Limpach, *ibid.*, 726).

By Nietzki's process a crystalline substance is obtained when the sulphonation product is mixed with 3 parts of ice, which is considered to be the 2 : 3-sultone  $C_{10}H_4(SO_3H)_2\left\langle\begin{matrix}O\\ |\\ SO_2\end{matrix}\right.$, convertible by alkalis into the trisulphonic acid,

The acid is used for making Ponceau 5R and 6R.

DIHYDROXYNAPHTHALENES AND THEIR SULPHONIC ACIDS.

1 : 5-DIHYDROXYNAPHTHALENE,



One hundred kilos. of sodium naphthalene-1 : 5-disulphonate or 120 kilos. of sodium 1-naphthol-5-sulphonate are heated with 300–400 kilos. of sodium hydroxide in a cast iron pan at 220–260° or at the same temperature in an autoclave with the addition of sufficient water to give a pasty mass. The following test is made. Five grams of the melt are dissolved in 200 c.c. of water and the solution is divided into 2 parts which are filtered and cooled. About 7 grams of sodium hydrogen carbonate are added to one half until a slight turbidity appears. Then a solution of tetrazotised benzidine is run in until the clear rim of a drop placed on filter paper is coloured pale brown when a drop of a solution of sodium naphthionate is brought into contact with it. The other half of the solution (100 c.c.) is now added and then 10 grams of sodium hydrogen carbonate. If the fusion is complete the whole dye must separate in blue flocks; the solution must not be coloured violet.

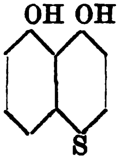
When this point is reached the fusion is dissolved in the calculated amount of dilute hydrochloric or sulphuric acid and, on cooling, the dihydroxynaphthalene separates in almost white flocks (Ewer and Pick, G.P., 41934; compare Bernthsen and Semper, *Ber.*, 1887, **20**, 938).

It is also obtained when 1 : 5-naphthylenediamine is heated with 4 per cent. hydrochloric acid under pressure at 180° (Aktiengesellschaft für Anilinfabrikation, G.P. Anm. A., 4029).

1 : 5-Dihydroxynaphthalene crystallises from water in scales melting at 265°.

It is used for making Diamond black PV.

1 : 8-DIHYDROXYNAPHTHALENE-4-SULPHONIC ACID, (S ACID)



Preparation from 1-Naphthol-4 : 8-disulphonic Acid.—The sodium salt of this acid is added to 3 parts of sodium hydroxide at about 250° and the melt maintained at this temperature until a sample, dissolved in water, no longer exhibits the fluorescence due to the naphtholdisulphonic acid and no increase in the amount of azo-dye produced with a diazo-compound in acetic acid solution is observed. By dissolving the melt in so much hydrochloric acid as will produce a saturated salt solution, the acid sodium salt of the dihydroxynaphthalenesulphonic acid is precipitated. The fusion is more advantageously carried on in an autoclave, in which case a 20–30 per cent. solution of sodium hydroxide is used (Farbenfabriken vorm. F. Bayer & Co., E.P., 13665 of 1889; G.P., 67829; U.S.P., 444679).

Preparation from 1-*Naphthylamine*-4 : 8-*disulphonic Acid.*—Fifty kilos. of the sodium salt of this acid are heated with 150 kilos. of 60 per cent. sodium hydroxide solution in an autoclave for twenty-four hours at 250°. The product is dissolved in 500 kilos. of hydrochloric acid (18 per cent.) and the solution allowed to cool, whereby the dihydroxy-acid crystallises out almost completely (Farbenfabriken vorm. F. Bayer & Co., E.P., 1227 of 1894; G.P., 71836).

In this process 1-amino-8-naphthol-4-sulphonic acid is an intermediate product and the dihydroxy-acid can be obtained from it by heating 1 part with 2 parts of sodium hydroxide and 0·2 part of water at 220–250° until ammonia is no longer observed. The melt is then worked up as above (Farbenfabriken vorm. F. Bayer & Co., G.P., 80315).

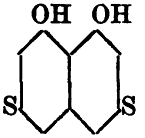
The acid can also be obtained from 1 : 8-naphthylenediamine-4-sulphonic acid by heating 24 parts with 400 litres of water and 20 kilos. of quicklime in an autoclave for six hours at 220–240°. On cooling, the ammonia is allowed to escape through the valve, and the cold liquid is filtered from calcium hydroxide and acidified. It is evaporated to one-third its bulk and saturated with salt to obtain the sodium salt of the dihydroxy-acid (Cassella & Co., G.P., 75962).

Preparation from 1-*Amino*-8-*naphthol*-4-*sulphonic Acid.*—23·9 Kilos. of the acid are stirred with 60 litres of water in an enamelled pan and exactly neutralised with sodium hydroxide. One hundred and eighty kilos. of sodium hydrogen sulphite (40° Bé.) are added and the mixture is heated for twenty-four hours at 90° until a sample, on acidifying, gives only a very small amount of unchanged amino-acid. The solution is then acidified, filtered from any unchanged amino-acid, rendered alkaline with sodium hydroxide and boiled to expel ammonia, then acidified with hydrochloric acid and boiled to remove sulphur dioxide, and the solution neutralised and used direct, or salt is added to it to precipitate the dihydroxy-acid (Farbenfabriken vorm. F. Bayer & Co., E.P., 16807 of 1899; F.P., 292882; G.P., 109102).

The salts of the acid are all readily soluble.

It is used for making Azo acid blues, Azo fuchsine B and G (Fast fuchsine G), Brilliant geranine, Victoria black B, Diamond green, and Brilliant azurine 5G.

1 : 8-DIHYDROXYNAPHTHALENE-3 : 6-DISULPHONIC ACID,
(CHROMOTROPE ACID)



Preparation from 1-*Naphthol*-3 : 6 : 8-*trisulphonic Acid.*—17·9 Parts of a paste containing 6·65 parts of the sodium salt of this acid or of the corresponding sultone (p. 221) are added at 100° to 13·5 parts of sodium hydroxide solution (60 per cent.) and the mixture is heated at 170–220° until the foaming has stopped. The melt is dissolved in water and acidified with hydrochloric acid, when, on cooling, the chromotrope acid separates out (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 13443 of 1890; G.P., 67563; compare also Koch, E.P., 9258 of 1890; G.P., 56058; Farbenfabriken vorm. F. Bayer & Co., E.P., 17141C of 1893; F.P., 237872; G.P., 80741; U.S.P., 563382).

Preparation from 1-*Amino*-8-*naphthol*-3 : 6-*disulphonic Acid* (*H Acid*).—Fifteen kilos. of the sodium salt are dissolved in 150 kilos. of 5 per cent. sodium hydroxide solution and heated in an autoclave for eight hours at 265°, the pressure being 22·5 atmospheres. The product is boiled to remove ammonia and then acidified, when the acid sodium salt of chromotrope acid separates out. Alternatively, one of the alkali salts of H acid can be heated with 10 parts of water for eight hours at 260–280°.

It is not necessary to isolate the H acid, but the melt in which the latter has been produced (p. 237) can be diluted to the right concentration with water and then again heated under pressure (Farbenfabriken vorm. F. Bayer & Co., E.P., 11522 of 1892; F.P., 222119; G.P., 68721).

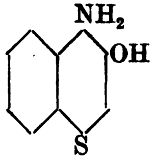
The acid can also be obtained by subjecting 1 : 8-naphthylenediamine-3 : 6-disulphonic acid to the same process as that just described (*idem*, E.P., 11522 of 1892; G.P., 69190) or by heating it (34 kilos.) with water (100–150 litres) in an autoclave for ten to twelve hours at 150–160° (Cassella & Co., G.P., 75153).

The disodium salt crystallises with $2H_2O$ and is readily soluble in water.

Chromotrope acid is used for making Chromotrope 2R, 2B, 6B, 8B, 10B, Victoria violet 4BS, Chromazone red A, Azo-alizarine black I, and Dianil blue R, 2R and B.

AMINONAPHTHOLSULPHONIC ACIDS.

1-AMINO-2-NAPHTHOL-4-SULPHONIC ACID,



This is prepared by the action of sulphurous acid on α-nitroso-β-naphthol (Böniger, *Ber.*, 1897, **27**, 23). A fine paste of nitroso-β-naphthol (containing 6–7 per cent.) is mixed with 3–4 parts (calculated on dry nitroso-β-naphthol) of cold sodium hydrogen sulphite solution (40 Bé.). The pale yellow solution is acidified with 3–4 parts of hydrochloric acid (21° Bé.), the free sulphurous acid effecting simultaneous sulphonation and reduction. The temperature is kept between 30° and 40°. The aminonaphthol-sulphonic acid separates out on cooling and is filtered off, washed, and dried.

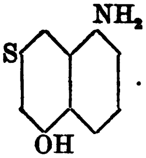
It may also be obtained by dissolving the nitrosonaphthol in sodium hydroxide and reducing the boiling solution with sodium hyposulphite (hydrosulphite). The product is acidified with acetic acid (Grandmougin, *Ber.*, 1906, **39**, 2497).

Tomioka (*Kogyo-Kwagaku-Zasshi* [*J. Chem. Ind., Tokyo*], 1917, **20**, 577) has prepared the acid by fusing with sodium hydroxide the 1-naphthylamine-2 : 4-disulphonic acid obtained by heating α-nitronaphthalene with sodium hydrogen sulphite solution, and also by reducing Orange II with stannous chloride or zinc dust and hydrochloric acid, treating the 1-amino-2-naphthol with bleaching powder, and acting on the resulting β-naphthaquinone-α-chloroimide with sodium hydrogen sulphite solution.

The acid is almost insoluble in cold water and very sparingly soluble in hot water. The sodium salt is sparingly soluble in hot water (compare Friedländer and Reinhardt, *Ber.*, 1897, **27**, 241).

The acid is used for making Palatine chrome black 6B (Salicin blacks) and Eriochrome blue black B.

1-AMINO-5-NAPHTHOL-7-SULPHONIC ACID, (M ACID)



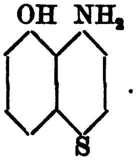
One hundred and fifty parts of sodium hydroxide and 50 parts of water are heated to 170°, 50 parts of the acid sodium salt of 1-naphthylamine-5 : 7-disulphonic acid are added and the mixture is kept at 160–220° for an hour or until a sample, dissolved in water, acidified, and cooled, shows no increase in the amount of aminonaphtholsulphonic acid formed. The melt is poured or ladled out on to trays, broken up when cold, and added to a mixture of 450 parts of ice and 600 parts of hydrochloric acid (30 per cent.). The aminonaphtholsulphonic acid is then filtered off and dried (Badische Anilin- & Soda-Fabrik, E.P., 2370 of 1893 ; G.P., 73276).

The acid may also be obtained by heating 1 : 5-diaminonaphthalene-7-sulphonic acid with water under pressure at 160° (Cassella & Co., G.P., 85058), by heating 1 : 5-dihydroxynaphthalene-7-sulphonic acid with ammonium sulphite and ammonia (Badische Anilin- & Soda-Fabrik, E.P., 1387 of 1900 ; F.P., 297464, 304820 ; G.P., 117471), and by heating 1-amino-5-naphthol-2 : 7-disulphonic acid with 10 per cent. sulphuric acid under pressure at 135° (Cassella & Co., G.P., 188505).

The acid and sodium salt form sparingly soluble leaflets.

It is used for making Oxamine blue B and Oxamine maroon.

1-AMINO-8-NAPHTHOL-4-SULPHONIC ACID, (S ACID)



Sodium 1-naphthylamine-4 : 8-disulphonate (p. 200) is melted with 3 parts of sodium hydroxide and a little water at 200–230° until a sample, dissolved in water and acidified with hydrochloric acid, shows no increase in the amount of aminonaphtholsulphonic acid formed. The melt is dissolved in 3 per cent. hydrochloric acid, boiled to expel sulphur dioxide, and the hot solution filtered. The aminonaphtholsulphonic acid separates out and is filtered off (Badische Anilin- & Soda-Fabrik, E.P., 20275 of 1891 ; addition to F.P., 206501 ; G.P., 63074).

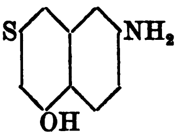
Another recipe is as follows: Sodium 1-naphthylamine-4 : 8-disulphonate is heated with 4–5 parts of potassium hydroxide and 1 part of water in an open or closed vessel at a temperature not exceeding 200° until the melt is clear and fluid and a sample diluted with water shows the characteristic bluish-green fluorescence of the aminonaphtholsulphonic acid. The mass is then poured into twice its bulk of water and faintly acidified with hydrochloric acid, when the aminonaphtholsulphonic acid separates out (Farbenfabriken vorm. F. Bayer & Co., G.P., 75317).

The acid is also obtained by dissolving 238 parts of 1 : 8-naphthylenediamine-4-sulphonic acid in 1,000 parts of water and the requisite amount of sodium carbonate and adding 2,000 parts of sodium hydrogen sulphite (40° Bé.) and 60 parts of acetone. The mixture is heated to 60–65° for about half an hour and then to 95–100° for two to three days or until a sample dissolves easily in dilute hydrochloric acid. The product is acidified with hydrochloric or sulphuric acid, the sulphur dioxide expelled by boiling, sodium hydroxide or carbonate added to decompose the sulphurous acid ester, and the alkaline liquid acidified, when 1-amino-8-naphthol-4-sulphonic acid is precipitated (Badische Anilin- & Soda-Fabrik, E.P., 16921 of 1900; F.P., 303241; G.P., 120016).

The acid is almost insoluble in cold water and very sparingly soluble in hot. The alkali salts are readily soluble.

It is used for making Buffalo black PY (Palatine black A, Wool black 4B, 6B), Columbia blue G and R, Benzocyanine B, 3B, and R, Benzo blue 2R, Chicago blue R, B, and 4B, Columbia black green D, and Columbia green.

2-AMINO-5-NAPHTHOL-7-SULPHONIC ACID, (J ACID)

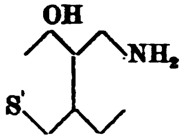


This is prepared by melting 2-naphthylamine-5 : 7-disulphonic acid with 3 parts of sodium hydroxide and 0·6 part of water at 170–180° or by heating it with 50 per cent. sodium hydroxide solution to 180–195° in an autoclave (Badische Anilin- & Soda Fabrik, E.P., 2614 of 1893; F.P., 227892; G.P., 75469; U.S.P., 521096).

The acid is sparingly soluble, and the alkali salts readily so.

It is used for making Benzo fast scarlets, Oxydiamine violet BF, Oxamine red, and Oxamine blue 4R.

2-AMINO-8-NAPHTHOL-6-SULPHONIC ACID,
(γ ACID)

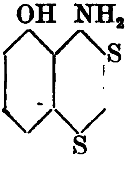


Sodium 2-naphthylamine-6 : 8-disulphonate is heated with about twice its weight of 50 per cent. sodium hydroxide solution for six hours at 185° (the English patent gives 190–195°). The melt is diluted with water and the γ acid precipitated by adding hydrochloric acid (Cassella & Co., E.P., 16699 of 1889 ; G.P. Anm. C., 3063 ; U.S.P., 454645. The temperature, 230–280°, given by Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 15176 of 1889 ; F.P., 201467, 201743 ; G.P., 53076, is too high, and the German patent was declared void).

The acid is very sparingly soluble, but the alkali salts dissolve readily.

It is used for making Neutral grey G, Nyanza black B, Diphenyl fast black, Benzo fast rose 2BL, Direct violet R (Dianol violet N), Diamine black BO, RO, and HW, Diamine brown V, Zambesi brown G, Benzo fast red 9BL, Diazine black H extra (Diamine black BH, Oxamine black BHN), Naphthamine black RE, Direct fast red F (Dianol fast red F), Direct brown 3RB (Diamine brown M), Indazurine TS, Panama black F (Columbia black FF, Dianol black FF), Isodiphenyl black R, Direct indigo blue BK, Direct black V, and Chloramine blue HW.

1-AMINO-8-NAPHTHOL-2 : 4-DISULPHONIC ACID,
(2 S ACID)

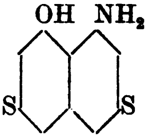


Sodium 1 : 8-naphthasultam-2 : 4-disulphonate (p. 201) is melted with 2½ parts of sodium hydroxide and 0·2 part of water at 170°. When a sample, treated with a diazo-compound, shows no increase in the amount of azo-dye formed, the melt is dissolved in water and acidified with hydrochloric acid. The acid sodium salt of the aminonaphtholdisulphonic acid separates out and can be purified by recrystallisation from water (Farbenfabriken vorm. F. Bayer & Co., E.P., 4979 of 1893 ; G.P., 80668 ; Aktiengesellschaft für Anilinfabrikation, E.P., 2984 of 1893 ; F.P., 228397 ; G.P. Anm. A., 3346 ; Dressel and Kothe, *Ber.*, 1894, **27**, 2141).

The acid is readily soluble. The acid sodium salt crystallises with $1H_2O$ and is readily soluble.

It is used for making Dianol brilliant blue 6B (Brilliant benzo blue 6B, Chicago blue 6B) and Chicago blue 4B and RW.

1-AMINO-8-NAPHTHOL-3 : 6-DISULPHONIC ACID, (H ACID)



Sodium 1-naphthylamine-3 : 6 : 8-trisulphonate (p. 202) is fused with 2 parts of sodium hydroxide and a little water at 180–190° until the melt becomes clear and fluid and a sample dissolved in water shows a bluish-red fluorescence. The melt is dissolved in water and the solution acidified with hydrochloric acid, when the acid sodium salt of H acid separates out.

The sodium salt of the trisulphonic acid may also be heated in an autoclave with 1–2 parts of sodium hydroxide solution (30–40 per cent.) to about 210°. The melt is then worked up as above (Farbenfabriken vorm. F. Bayer & Co., E.P., 13443 of 1890 ; addition to F.P. 201467 ; G.P., 69722 ; U.S.P., 540412).

This method is the one generally used for making H acid.

Another method, formerly employed to some extent, was to dinitrate naphthalene-2 : 7-disulphonic acid (or the sulphonation mixture containing this together with some of the 2 : 6-disulphonic acid), to reduce the 1 : 8-dinitronaphthalene-3 : 6-disulphonic acid so produced, and to heat the diamino-acid with 10 per cent. sulphuric acid at 100–120° or with 40 per cent. sodium hydroxide at 200° (Cassella & Co., E.P., 1742 of 1891 ; F.P., 210950 ; G.P., 67062). The azimino-compound of the diamino-acid may also be heated with 80 per cent. sulphuric acid at 170° (*idem*, G.P., 69963), or the dinitro-acid can be heated with sodium hydrogen sulphite solution at 90–100° (Farbenfabriken vorm. F. Bayer & Co., E.P., 21138 of 1899 ; F.P., 294164 ; G.P., 113944).

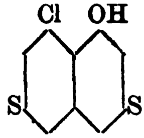
1-Chloro-8-naphthylamine-3 : 6-disulphonic acid also yields H acid when fused with sodium hydroxide (Badische Anilin- & Soda-Fabrik, G.P., 147852).

The acid is sparingly soluble in cold water ; the acid sodium salt crystallises with $1\frac{1}{2}H_2O$ and is sparingly soluble.

H acid is used for making a very large number of azo-dyes, for example, Lanacyl violet B, Lanacyl blue 2B, Sulphone acid blues,

Naphthol blue black (Buffalo black NB, Naphthylamine black 10B, Agalma black 10B, Acid black, Wool black, Coomassie blue black), Buffalo black 10B, Diazine black H extra (Diamine black BH, Oxamine black BHN), Benzocyanine B, 3B, and R, Niagara blue 2B, 3B. BX (Benzo blue 2B, 3B, BX), Niagara blue 4B (Benzamine pure blue, Diamine sky blue,) Indazurine 5GM, Benzo olive, Diamine bronze, Erie direct black GX and RX (Union black, Cotton black, Direct deep black), Palatine chrome green G (Chrome fast green G), Erie direct green ET, Diphenyl green G and 3G, Chloramine black N, Chloramine green B, Chloramine blues, Dianol green B (Diamine green B, Oxamine green B), and Erie direct green (Dianol green G, Diamine green G).

1-Chloro-8-naphthol-3 : 6-disulphonic Acid,



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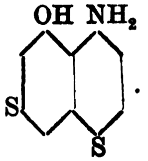
Fifty kilos. of 1-amino-8-naphthol-3 : 6-disulphonic acid (H acid) are dissolved in water with the addition of sodium carbonate, the solution is cooled with ice, and hydrochloric acid added in sufficient quantity to keep the whole acid throughout the subsequent operation of diazotising with the calculated amount of sodium nitrite dissolved in a little water. The yellow diazo-compound is filtered off, mixed with 10 per cent. hydrochloric acid, cooled to 10°, and a solution of 5 kilos. of cuprous chloride added. The mixture is then heated at 100° until the yellow colour has disappeared and all is in solution. The copper is precipitated with hydrogen sulphide, the copper sulphide filtered off, and the boiling filtrate is saturated with salt. On cooling, the acid sodium salt of the chloro-acid separates and is filtered off and dried (Cassella & Co., E.P., 1920 of 1894 ; F.P., 235271 ; G.P., 79055 ; U.S.P., 535037).

It is also formed from 1 : 8-naphthylenediamine-3 : 6-disulphonic acid by treating it with sodium nitrite in acid solution and acting on the resulting azimino-compound with copper paste. The 1-chloro-8-naphthylamine-3 : 6-disulphonic acid produced is converted into the naphthol acid by heating it with dilute sulphuric acid under pressure (Badische Anilin- & Soda-Fabrik, G.P., 147852).

The neutral salts of the acid are very readily soluble in water; the acid salts crystallise well.

The acid is used for making Diamine brilliant blue G.

1-Amino-8-naphthol-4 : 6-disulphonic Acid,
(K Acid)

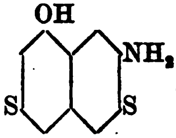


Two hundred kilos. of sodium 1-naphthylamine-4 : 6 : 8-trisulphonate are heated with 300 kilos. of sodium hydroxide and 120 kilos. of water in an autoclave at 170–175° until a sample shows a blue fluorescence and the formation of an azo-dye with a diazo-compound either in alkaline or acetic acid solution does not increase. On cooling, the melt is dissolved in water and acidified with hydrochloric acid, when the acid sodium salt of the aminonaphtholdisulphonic acid gradually separates (Farbenfabriken vorm. F. Bayer & Co., E.P., 17141C of 1893; F.P., 237872; G.P., 80741; U.S.P., 563382).

According to Kalle & Co. (E.P., 515 of 1894; G.P., 93700, 99164; U.S.P., 563383, 563384), the acid sodium salt of 1-naphthylamine-4 : 6 : 8-trisulphonic acid (obtained from 10 parts of sodium naphthalene-1 : 5-disulphonate) is heated with 15 parts of sodium hydroxide and 5 parts of water at 140–200°; towards the end, the colour changes from yellow to reddish-brown; the product is dissolved in 200 parts of water and the acid sodium salt of the aminonaphtholdisulphonic acid precipitated by hydrochloric acid. The acid sodium salt is readily soluble.

It is used for making Blue black N, Chrome patent green, Naphthamine black RE, and Naphthamine blues.

2-Amino-8-naphthol-3 : 6-disulphonic Acid,
(2 R Acid)

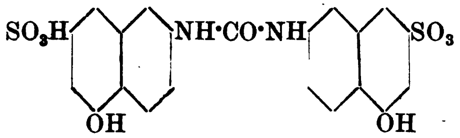


One hundred kilos. of sodium 2-naphthylamine-3 : 6 : 8-trisulphonate are mixed with 200 kilos. of sodium hydroxide and 50 kilos. of water and heated to 220-260°. The reaction begins at 200–210° and can be brought to completion by heating to 230° for twelve to eighteen hours, but proceeds more rapidly at higher temperatures. On raising the temperature to 240–260° the melt becomes red and foams vigorously. After fifteen to thirty minutes the foaming is over and the mass becomes thick. It is now dissolved in water and acidified with hydrochloric acid, when the acid sodium salt of the aminonaphtholdisulphonic acid separates out (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 15175 of 1889; F.P., 201742; G.P., 53023).

The acid and salts are readily soluble.

It is used for making Direct black V, Direct indone blue R, Trisulphone brown B,G, and GG, and Columbia black B and R.

5:5′-DIHYDROXY-7:7′-DISULPHO-2:2′-DINAPHTHYLCARBAMIDE,

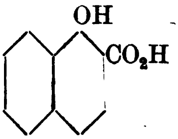


23·9 Parts of 2-amino-5-naphthol-7-sulphonic acid (J acid) are dissolved in 150–200 parts of water and a solution of 24 parts of sodium carbonate, and a stream of carbonyl chloride (phosgene) is passed through the solution at the ordinary temperature, the whole being kept alkaline and well stirred. The stream of gas is stopped when a sample, treated with dilute hydrochloric acid, gives no precipitate of unchanged J acid and is not changed by the addition of sodium nitrite. The solution is acidified with hydrochloric acid and the compound salted out, filtered off, pressed and dried (Farbenfabriken vorm. F. Bayer & Co., E.P., 3615 of 1900; F.P., 297367; G.P., 116200; U.S.P., 656646).

The substance is readily soluble in water or dilute acids. It is used for making Benzo fast scarlets.

NAPHTHOLCARBOXYLIC ACIDS.

1-HYDROXY-2-NAPHTHOIC ACID,

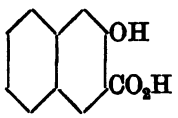


Sodium α-naphthoxide is submitted to the action of the calculated amount of carbon dioxide under pressure at 120–145°. (See under Salicylic acid, p. 149.) The dry product is dissolved in water, the free acid precipitated by hydrochloric acid, and purified by recrystallisation (Heyden, E.P., 8155 of 1886; F.P., 176871; G.P., 38052).

The acid crystallises in needles melting at 187° and dissolves in about 1,720 parts of water at 17°. The sodium salt crystallises with 1H_2O and is readily soluble in hot water.

It is used for making 1:7-dihydroxy-2-carboxynaphthalene-4-sulphonic acid.

2-HYDROXY-3-NAPHTHOIC ACID,

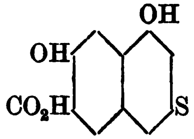


Sodium β-naphthoxide is submitted to the action of the calculated quantity of carbon dioxide under pressure at 200–250°. (See under Salicylic acid, p. 149.) The dry product is dissolved in water, the free acid precipitated by hydrochloric acid, and purified by recrystallisation (Heyden, E.P., 9612 of 1889; F.P., 198811; G.P., 50341; U.S.P., 410295; this gives the temperature 200–215°).

The acid crystallises in yellow scales melting at 216° and is only sparingly soluble in hot water.

It is used for making nigrotic acid and for Brilliant lake red R, Lithol rubine B, and Lake Bordeaux B.

1 : 7-DIHYDROXY-6-CARBOXYNAPHTHALENE-3-SULPHONIC ACID,
(NIGROTIC ACID)



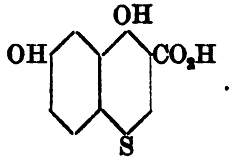
2-Hydroxy-3-naphthoic acid is added to 4 parts of fuming sulphuric acid (containing 24 per cent. of sulphur trioxide) and the mixture heated to 125–150° for two to three hours. The mass is then poured into water, neutralised with milk of lime, and the sodium salt prepared in the usual way. The solution is evaporated until the disulphonate separates out.

This sodium salt is then heated with 2 parts of sodium hydroxide for two to three hours at 210–220°, and finally at 230–240°. The reaction is at an end when the melt, fluid at the beginning, becomes solid and a sample dissolved in water and acidified with hydrochloric acid shows no increase in the amount of the precipitate formed. The melt is then dissolved in water and acidified, when the acid sodium salt of nigrotic acid separates out (Society of Chemical Industry in Basle, E.P., 14161 of 1892; F.P., 219875; G.P., 67000).

The acid forms pale yellow needles readily soluble in water.

It is used for making Direct violet R, Direct indigo blue BN Direct grey B and R, and Direct blue B and R.

1 : 7-Dihydroxy-2-carboxynaphthalene-4-sulphonic Acid,



1-Hydroxy-2-naphthoic acid is stirred into 4 parts of fuming sulphuric acid containing 20 per cent. of sulphur trioxide, the mixture being cooled. When the addition is finished, the whole is warmed slowly to the temperature of the water-bath. The mass becomes thick at first, but thin after further warming; finally it becomes thick again. It is then dissolved in the requisite amount of hot water to dissolve it, and, on cooling, the disulphonic acid crystallises out (Seidler, G.P., 56328).

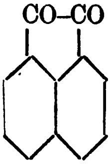
For the fusion, 200 kilos. of sodium hydroxide are dissolved in 50 litres of water and the solution is evaporated until, at 190°, just sufficient water is present to keep the melt liquid. Fifty kilos. of the acid sodium salt of the above disulphonic acid are added and the mixture is kept at 190–200° for four to five hours. The water which evaporates during this time must be replaced so as to avoid solidification of the melt. The product is dissolved in about 1,000 litres of water, acidified with hydrochloric acid, and filtered. The acid sodium salt of 1 : 7-dihydroxy-2-carboxynaphthalene-4-sulphonic acid crystallises from the solution and can be purified by recrystallisation (Basle Chemical Works, Bindschedler, E.P., 4630 of 1894; F.P., 236723; G.P., 84653).

Friedländer and Zinberg (*Ber.*, 1896, 29, 38) melt the disulphonic acid with 4 parts of sodium hydroxide at 220–240° and obtain 50–60 per cent. of the disulphonic acid employed.

The acid sodium salt is sparingly soluble in water, but the neutral sodium salt is readily so.

It is used for making Indazurine RM, TS, GM, 5GM, and BB.

Acenaphthenequinone,



Fifty kilos. of acenaphthene are dissolved in 250 kilos. of amyl alcohol in a vessel provided with a reflux condenser, a gas supply pipe, and a tap funnel. The boiling solution is saturated with hydrogen chloride, and while the gas is passed through the solution, 152 kilos. of amyl nitrite are introduced drop by drop through the tap funnel during about an hour. Nitrous gases are evolved and boiling is continued until the evolution has ceased. The liquid is at first violet, but becomes yellowish-red. It is mixed with water and the amyl alcohol distilled off with steam. The residue forms a slightly red, soft mass which is dissolved by trituration with sodium hydroxide solution. A little oil, a red substance, and sometimes small amounts of unchanged acenaphthene, remain undissolved in the solution. The alkaline solution is thoroughly shaken with animal charcoal, filtered, and precipitated with carbon dioxide; a voluminous yellow to reddish-yellow precipitate at first separates out, which soon becomes of a sandy, crystalline nature. The filtrate of the oxime, on the addition of hydrochloric acid, yields naphthalic acid (Kalle & Co., E.P., 19341 of 1910; F.P., 419379; G.P., 228698; Reissert, *Ber.*, 1911, **44**, 1749).

The product obtained as described above, which is probably acenaphthenequinonemonoxime, is frequently accompanied by an isomeride which on heating with 70 per cent. sulphuric acid does not, like the oxime, decompose into acenaphthenequinone and hydroxylamine, but yields naphthalic anhydride and ammonia. It can be isolated by stirring 10 kilos. of the mixture with 300 litres of hot water and adding 60 kilos. of sodium sulphite and 5 kilos. of ammonium chloride and heating the whole for about three hours at about 90°. The isomeride is isolated by filtering, and is pressed and dried. For the purpose of making dyes it is not necessary to separate the two products (*idem*, E.P., 19340 of 1910; F.P., 419379; compare also G.P., 232714, 233473).

The oxime is converted into the quinone by heating it with 7 parts of 75 per cent. sulphuric acid at 100° for an hour. The solution is diluted with water, filtered, and the residue digested with warm dilute sodium hydroxide solution.

Acenaphthenequinone, which was isolated by Graebe and Gfeller (*Ber.*, 1892, **25**, 652; *Annalen*, 1893, **276**, 1) by oxidising acenaphthene with chromic acid, forms yellow needles melting at 262–263°, and soluble in benzene or acetic acid.

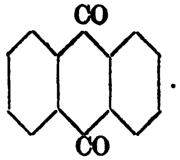
The oxime melts at 220°.

It is used for making Ciba scarlet G, Ciba red R, and Ciba orange G.

ANTHRACENE SERIES.

ANTHRAQUINONE AND ITS DERIVATIVES.

ANTHRAQUINONE,



Anthraquinone is manufactured by oxidising anthracene with chromic acid, according to the equation:

$$C_{14}H_{10}+Na_2Cr_2O_7+4H_2SO_4= C_{14}H_8O_2+Cr_2(SO_4)_3+Na_2SO_4+5H_2O.$$

The oxidation is effected in lead-lined tubs of about 10–12 cubic metres' capacity (about 2,500 gallons) fitted with lead-covered agitators and direct steam pipes, also of lead. One hundred and fifty kilos. of sublimed anthracene are mixed with 3,000–4,000 litres of water and the mixture is heated to 75°; 2,000 litres of a solution containing 300 kilos. of sodium dichromate and 600 kilos. of sulphuric acid (66° Bé.) are now run in slowly, the temperature being gradually raised to about 95°. The oxidation requires twelve to sixteen hours, and it is important not to add the chromic acid solution too quickly or to work in a too concentrated solution, otherwise much frothing occurs.

Tests are made by filtering a sample, washing, and subliming it over a naked flame. With a little practice it is easy to distinguish the fine needles of anthraquinone from the silvery leaflets of anthracene. The absorption of the chromic acid can also be ascertained by titration with ferrous sulphate.

When the operation is finished, the contents of the tub are run into an egg and blown through a filter press, where the anthraquinone is thoroughly washed, the filtrate being collected in order to recover the chromium.

The yield from an anthracene of good quality is about 110 parts of anthraquinone from 100 parts of anthracene (Grandmougin, *Rev. prod. chim.*, 1917, **20**, 20).

The anthraquinone so obtained is purified by sublimation with superheated steam; the pan is heated by superheated water, and the sublimed anthraquinone condensed by means of a water-jet as shown in Fig. 25.

In the diagram on p. 245, 1 is a cast iron flanged pan, the flange of which supports it in the cast iron jacket, 2, which serves as a metal-bath built over the fire-grate, 14. The pan may be heated in the way indicated, but the more modern process is to enclose it in a tight-fitting water-jacket containing steam tubes through which passes superheated steam to superheat the water in the jacket. In this case, the jacketed pan rests on top of the furnace in which the steam is superheated. The pan is closed by the lid, 3, in which is a manhole, 4, an opening for a thermometer, 16, and a second opening for a safety-cork, 13. The side opening, 5, is united with the copper condensing pipe, 6, in the vertical branch of which is fixed the water-pipe, 17, ending in the spray, 7. The lower part of this vertical branch passes below the lid, 8, into the wooden box, 9, fitted with a perforated bottom, 11, covered with filter-cloth.

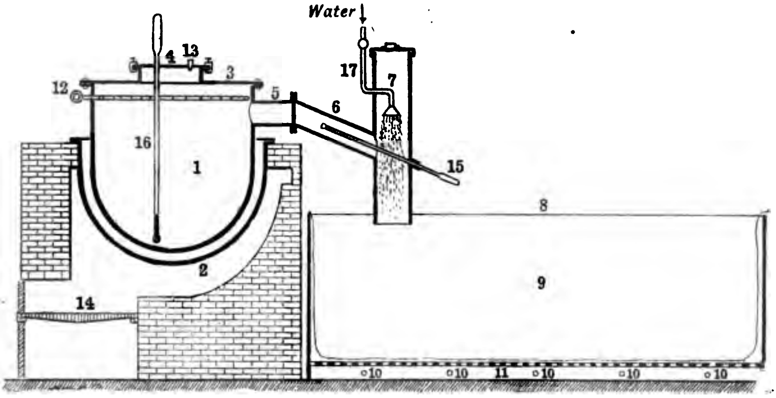


FIG. 25.

After the anthraquinone has been filled into the pan, the bath is heated until the temperature inside the pan is about 320°; then steam at about 240–260° is passed in through the perforated iron pipe, 12. The vapours are condensed in 6 by means of a fine but powerful water-spray. The water flows through the filter, under the perforated bottom, and escapes to the drain through the holes, 10. If the condensing tube becomes stopped up, causing the pressure to rise in the pan, the safety-cork is blown out. The rod, 15, which passes through a stuffing-box (or simply a cork) serves to break any crusts that may form.

The sublimate on the filter is transferred to a vacuum filter and dried. The anthraquinone forms a yellow powder of at least 97·5–98 per cent. purity.

If an impure anthracene has been employed, the anthraquinone can also be purified by treatment with two to three times its weight of sulphuric acid at 100° until a sample, when poured into water, gives an almost white precipitate. The impurities are dissolved whilst the anthraquinone is unattacked. The mass is poured into water, filtered, and the anthraquinone washed with water and dilute sodium carbonate solution.

Other solvents, such as liquid sulphur dioxide (Farbenfabriken vorm. F. Bayer & Co., E.P., 5539 of 1892; F.P., 220621; G.P., 68474), aniline (Sadler & Co., E.P., 17635 of 1901; G.P., 137495) and pyridine, have been proposed. (For extraction plant, see Brönner, E.P., 759 of 1882; F.P., 149017; G.P., 21681.)

An electrolytic process for the oxidation of anthracene in a chromic acid bath has been patented by Darmstädter (G.P., 109012), and an almost quantitative yield of anthraquinone is stated to be obtained by the electrolytic oxidation of anthracene in 20 per cent. sulphuric acid in the presence of cerium sulphate (Farbwerke vorm. Meister, Lucius, & Brüning, E.P., 19178 of 1902; F.P., 328069; G.P., 152063; U.S.P., 729502, 757136).

Recovery of Chromium.—The chromium may be recovered by precipitating with sodium carbonate and converting the chromium hydroxide into acetate, fluoride, etc., which salts are used in the textile industry, or it may be converted into chrome alum by adding potassium sulphate. Another method consists in adding to the solution sufficient milk of lime to precipitate the free sulphuric acid, filtering from calcium sulphate, then precipitating chromium oxide by adding excess of milk of lime, and heating the precipitate in a reverberatory furnace in a current of air in order to obtain calcium chromate. This is then treated with sodium carbonate to obtain sodium chromate. The recovery may also be effected by electrolytic oxidation. The green liquors are first evaporated in a vacuum in an apparatus made of hard lead to such a concentration that, after oxidation, they can be used direct in the manufacture of anthraquinone. About 40 cells, consisting of narrow iron, lead-lined vessels, about 1·4 metres long and 1 metre high, are used, and the solution flows through the system from cell to cell until, finally, it emerges from the last one fully oxidised. The lead lining is connected with the positive pole, and strips of lead, hung in the vessels, are connected with the negative pole. In order to regenerate 200 kilos. of the dichromate, necessary to oxidise 100 kilos. of anthracene, reckoning an 80 per cent. yield, about 500 kilowatt-hours are required at 3·6 volts.

Ferric sulphate has also been proposed as an oxidising agent

(Société Anonyme des Matières Colorantes et Produits Chimiques de St. Denis, E.P., 8431 of 1887).

Several processes have been described for the preparation of anthraquinone by oxidising anthracene with oxides of nitrogen or nitric acid. Thus the Chemische Fabrik Grünau, Landshoff, & Meyer (G.P., 215335) mixes anthracene (90 per cent.) with 2 parts of a compound of nitric oxide and zinc oxide (*idem*, G.P., 207170) and heats the mixture in a sublimation apparatus in a mild stream of air or oxygen. The temperature is raised quickly to 250–350° and maintained for three to four hours. The anthraquinone sublimes on the cooler part of the apparatus, and the zinc residues are easily removed.

In a later patent (E.P., 16312 of 1909 ; G.P., 234289) the same firm claims the production of anthraquinone by the action of nitric oxide and air, or nitrogen peroxide, on anthracene at 200° or (G.P., 254710) on a mixture of anthracene and pumice stone or asbestos powder at 100–200°.

The Farbwerke vorm. Meister, Lucius, & Brüning (G.P., 256623) states that a mixture of nitro-compounds is obtained by the above process (G.P., 234289) and proceeds as follows : 100 parts of anthracene are mixed with 200 parts of pumice stone (or asbestos powder or glass wool) and 100 parts of zinc dust (or lead oxide) and the whole is packed into a vertical reaction tower. The mass is covered with a mixture of 200 parts of pumice stone and 100 parts of zinc dust. At 75–100° a dry mixture of air and nitrogen peroxide (10 per cent.) is led into the bottom of the tower, and the oxidation is finished after nine hours. The temperature is now raised to 280°, and the anthraquinone is sublimed in a brisk current of air containing 1 per cent. of nitrogen peroxide, and collects in the upper part of the tower. The yield is 94–95·5 per cent. of the theoretical (of 94–96·8 per cent. material) and the loss of nitrogen peroxide is 0·5–1·5 per cent. Alternatively, 1–10 parts of molybdenum oxide may be added to the mixture, in which case the oxidation is complete in six to seven hours. and the yield is 96–98 per cent. of the theoretical (of 97·4 per cent. material).

In the following process the oxidation is carried on by means of nitrogen peroxide under entirely different conditions.

Thirty kilos. of nitrogen peroxide are mixed with 100 kilos. of nitrobenzene, and 25 kilos. of anthracene are added at a temperature of about 15° ; after remaining for some hours at the ordinary temperature, the mixture is slowly heated to about 100°, and, when the evolution of nitric oxide has ceased, is allowed to cool, and the anthraquinone filtered off and washed. The nitric oxide is reconverted into the peroxide for use in a further operation (Badische Anilin- & Soda-Fabrik, E.P., 11472 of 1910; F.P., 416735; G.P., 268049; U.S.P., 1083051).

Oxidation with Nitric Acid.—(1) One hundred and fifteen parts of anthracene (86 per cent.) are suspended in 210 parts of glacial acetic acid, and, at 15–20°, 175 parts of nitric acid (62 per cent.) are added and the mixture is stirred for two days at 15–20°. The crystals are filtered off and, while still moist, are mixed with 1,000 parts of nitrobenzene, 47 parts of nitric acid (40° Bé.) are added, and the whole is heated for four hours at 90–105°. After cooling, the crystals of anthraquinone are collected, washed with nitrobenzene and finally with benzene, and dried.

(2) One hundred and seventeen parts of anthracene (85 per cent.) are suspended in 300 parts of nitrobenzene and, at 30°, a solution of 3 parts of mercury in 460 parts of nitric acid (31 per cent.) is added during three hours. The solution is filtered and heated at 35° for a further three hours. The nitric acid is then separated, 360 parts (15·6° Bé.) being recovered. The nitrobenzene solution is treated with a solution of 5 parts of mercury in 55 parts of nitric acid (40° Bé.) and heated to 105° in the course of twenty-five minutes. The temperature then rises rapidly to 120°, and at about 110° chlorine is introduced for nearly ten minutes in order to remove organic compounds of mercury. After cooling, the anthraquinone is filtered off and washed as described above.

(3) In the first part of the operation in (2) 15 parts of mercury are used instead of 3 parts. After separating the nitric acid, a rapid stream of chlorine is led into the filtered nitrobenzene solution and it is heated to 100° in the course of about twenty minutes. The temperature is then raised to 110–120°, the stream of chlorine being uninterrupted until the end of the whole operation, and this temperature is maintained for some time. After cooling, the anthraquinone is collected (Chemische Fabrik Griesheim-Elektron, E.P., 12055 of 1914; F.P., 472216; U.S.P., 1119546; compare also U.S.P. 1103383, in which mercury is not employed).

Oxidation with Sodium Nitrate.—Twenty grams of anthracene are mixed with 23 grams of sodium nitrate and 80 grams of magnesium chloride, $MgCl_2,6H_2O$, and heated in an open vessel on the sand-bath. At 125°, anthraquinone is formed as shown by the yellow colour. The temperature is allowed to rise to 145°, the water which evaporates is replaced by the addition of 40 c.c., the mass is vigorously stirred, and heated slowly to 300°. The anthraquinone collects above the white layer of salts and for purification is mixed with 5 grams of magnesium oxide and sublimed. In this way, 18·9 grams of almost pure anthraquinone (96·8 per cent.) are obtained (Hofmann, Quoos, and Schneider, *Ber.*, 1914, **47**, 1992 ; G.P. Anm. H., 61262).

Oxidation with Oxygen.—One hundred parts of a 30 per cent. aqueous anthracene paste is mixed with 3,000 parts of water, 250 parts of 25 per cent. ammonia, and 5 parts of copper oxide in a vessel capable of resisting pressure, a quantity of oxygen corresponding with 3 atoms per mol. of anthracene, or the corresponding quantity of air, is forced in, and the mass is stirred and heated for two hours at 170°. After cooling, the anthraquinone is separated and freed from copper compounds by washing with ammoniacal water. Nickel, cobalt, iron, and lead compounds may be used as catalysts instead of copper oxide (Farbwerke vorm. Meister, Lucius, & Brüning, G.P., 292681). Another catalytic method consists in passing a mixture of anthracene vapour and air at 500° over vanadium pentoxide or molybdenum trioxide (The Selden Co. and Gibbs, E.P., 119518 [1917] ; U.S.P., 1285117). The oxidation of anthracene in sulphuric acid solution by means of ozonised air has been proposed by Heinemann (E.P., 5514 of 1915).

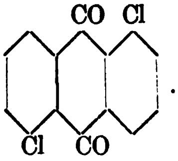
Anthraquinone is also produced by the action of sulphuric acid on *o*-benzoylbenzoic acid (Perkin, jun., *Trans.*, 1891, **59**, 1012) ; the preparation is described by Heller (*Zeitsch. angew. Chem.*, 1906, **19**, 669 ; *Ber.*, 1908, **41**, 3631). A mixture of 1 kilo. of phthalic anhydride, 3·5 kilos. of benzene, and 1·8 kilos. of aluminium chloride is introduced into a lead-lined pan provided with a stirrer and reflux condenser and heated by means of a hot-water jacket. At 30°, evolution of hydrogen chloride commences, and as the temperature rises the mass increases in viscosity until it eventually becomes so thick that it stops the stirrer. When 70° has been reached, the heating is continued at that temperature until the evolution of hydrogen chloride ceases. The mass is then cooled, diluted with 3–4 parts of water, the excess of benzene distilled off by means of steam, the residue rendered alkaline by the gradual addition of sodium hydroxide, and boiled for several hours to decompose the aluminium compound into alumina and to form the sodium salt of *o*-benzoylbenzoic acid, from the solution of which, after filtration, the acid is precipitated by acidification. The yield is 95–97 per cent. of the theoretical.

The *o*-benzoylbenzoic acid is converted quantitatively into anthraquinone when heated with 5–6 parts of sulphuric acid at 150° for an hour.

Anthraquinone melts at 285–286° and boils at 382°; it sublimes very easily. It is insoluble in water, sparingly soluble in alcohol or ether, but more readily so in hot glacial acetic acid. One hundred grams of benzene dissolve 0·256 gram at 20° and 1·775 grams at 80°. One hundred grams of chloroform dissolve 0·605 gram at 20° and 1·577 grams at 60° (Tyrer, *Trans.*, 1910, **97**, 1778), whilst 100 grams of alcohol dissolve 0·437 gram at 25° and 100 grams of ether dissolve 0·104 gram at 25° (Hildebrand, Ellefson and Beebe, *J. Amer. Chem. Soc.*, 1917, **39**, 2301).

It is the starting point for many derivatives (chloro-, nitro-, amino-, sulphonic, etc.) which are used for making Alizarin, Indanthrene, and other important vat dyes.

1 : 5-DICHLOROANTHRAQUINONE,



A solution of 5 grams of potassium anthraquinone-1 : 5-disulphonate in 150 c.c. of water and 40 c.c. of hydrochloric acid is heated to boiling and a solution of 10 grams of sodium chlorate gradually added, the whole being well stirred. In about two hours 3 grams (91 per cent. of the theoretical) of almost pure 1 : 5-dichloroanthraquinone separate (Ullmann and Knecht, *Ber.*, 1911, **44**, 3125).

The large scale adaptation of this is as follows: A solution of 20 kilos. of sodium anthraquinone-1 : 5-disulphonate in 400 litres of water and 40 kilos. of hydrochloric acid (20° Bé.) is heated to boiling and a solution of 40 kilos. of sodium chlorate in 300 litres of water added gradually. The mixture is kept boiling for some hours until the separation of 1 : 5-dichloroanthraquinone is complete (Farbenfabriken vorm. F. Bayer & Co., E.P., 1822 of 1908; F.P., 386599; G.P., 205195).

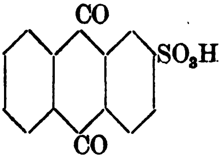
The compound can also be obtained by suspending 20 kilos. of 1 : 5-diaminoanthraquinone in 200 kilos. of hydrochloric acid and diazotising at 5–10° with 18 kilos. of sodium nitrite. The solution is then run slowly into a solution of 10 kilos. of cuprous chloride in 300 kilos. of hydrochloric acid, when the 1 : 5 dichloro-derivative separates out (*idem*, G.P., 131538).

1 : 5-Dichloroanthraquinone melts at 251° (corr.) and forms

citron-yellow needles which are very sparingly soluble in alcohol but readily so in boiling toluene.

It is used for making Indanthrene violet RN.

ANTHRAQUINONE-2-SULPHONIC ACID, (β ACID)



One hundred kilos. of anthraquinone are added to 100 kilos. of fuming sulphuric acid (containing 45–50 per cent. of sulphur trioxide) and the mixture is heated during the course of an hour to 160°. (Grandmougin, "Lehrbuch der Farbenchemie," 4th ed., 1913, p. 260, states that the β acid is almost exclusively formed by sulphonating with fuming acid containing 15 per cent. of sulphur trioxide at 150°.) The product is allowed to flow slowly into boiling water, the mixture boiled for some time, and the unchanged anthraquinone (20–25 per cent.) collected in a filter press, washed, and dried, to be used again. The filtrate is neutralised with sodium hydroxide and allowed to cool, when the greater part of the sodium salt ("silver salt") crystallises in white, silvery leaflets. By evaporation of the filtrate from this, a further quantity separates, and the silver salt is obtained pure by recrystallisation. If the mother liquor is further concentrated to 30° Bé., most of the sodium sulphate separates out, and if the filtrate from this is evaporated to dryness, in addition to sodium sulphate, some disulphonic acid is obtained.

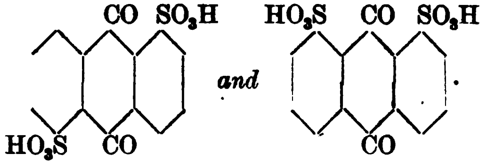
The Barrett Co. (U.S.P., 1260535) precipitates the "silver salt" by adding sodium sulphate and recovers the disulphonic acids from the filtrate.

Dünschmann (*Ber.*, 1904, **37**, 331) states that, after most of the "silver salt" has been removed, further evaporation gives a product containing a mixture of the 2 : 6-disulphonic acid with a little of the 1- and 2-sulphonic acids, and if a hot saturated solution of this is treated with one-tenth of its bulk of a 45 per cent. solution of sodium hydroxide and cooled to 50–55°, most of the 2 : 6-acid separates, leaving the 1-acid (sodium salt) in the mother liquor, from which it crystallises on cooling. The final mother liquor from the above product contains the 2 : 7-acid.

The free acid is readily soluble in water or alcohol. The sodium salt crystallises with $1H_2O$; 100 parts of water dissolve 5·59 parts at 18° and 18·88 parts at 100°.

It is used for making Alizarin.

ANTHRAQUINONE-1 : 5- *and* -1 : 8-DISULPHONIC ACIDS,



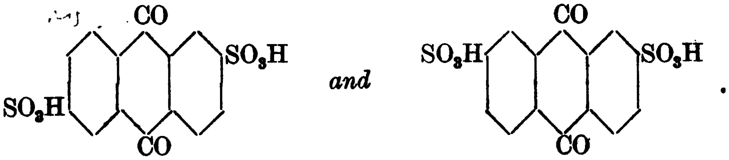
(1) One hundred parts of anthraquinone, 1 part of mercury and 200 parts of fuming sulphuric acid (containing 40 per cent. of sulphur trioxide) are heated slowly to 160° and kept at this temperature for an hour. The cooled, liquid mass is then stirred into about 900 parts of cold water, the solution neutralised with milk of lime, filtered from the calcium sulphate, and the calcium salts are converted into sodium salts. On evaporation, the sodium salt of the 1 : 8-acid (sometimes called the χ-acid) separates out first, and the large middle fraction consists of the 1 : 5-salt (sometimes called *p*) (Iljinsky, *Ber.*, 1903, **36**, 4194; Iljinsky and Wedekind & Co., E.P., 10242 of 1903 ; F.P., 332709).

(2) One hundred parts of anthraquinone are intimately mixed with 1 part of precipitated mercuric oxide (the United States patent gives mercurous sulphate) and added to 200 parts of fuming sulphuric acid (containing 44 per cent. of sulphur trioxide). The mixture is heated to 130°, when a vigorous reaction usually occurs. Care must be taken that the temperature does not rise above 150–160°, and heating is continued until a sample dissolves to a clear solution in water and practically all the free sulphur trioxide has disappeared. On cooling to 50° and after 75 parts of sulphuric acid (60° Bé.) have been added to the mixture, the crystals of the 1 : 5-acid, which separates quantitatively, are filtered on asbestos and washed with sulphuric acid (60° Bé.). It is purified by dissolving it in hot water and precipitating as potassium salt by adding potassium chloride. The filtered sulphuric acid solution is run into water, the solution is heated and on adding potassium chloride the potassium salt of the 1 : 8-acid is precipitated in pale yellow needles (Schmidt, *Ber.*, 1904, **37**, 66 ; Farbenfabriken vorm. F. Bayer & Co., E.P., 13808 of 1903 ; F.P., 333144 ; G.P., 157123 ; U.S.P., 742910).

The acids are also produced from the corresponding dichloroderivatives by treating them with sodium sulphite solution (Farbenfabriken vorm. F. Bayer & Co., G.P., 164292), and 5-nitroanthraquinone-1-sulphonic acid yields the 1 : 5-disulphonic acid by the same treatment (*idem*, G.P., 167169).

The 1 : 5-acid is used for making anthrarufin, 1 : 5-dichloroanthraquinone, etc.

ANTHRAQUINONE-2 : 6- *and* 2 : 7-DISULPHONIC ACIDS,
(α- *and* β-DISULPHONIC ACIDS)

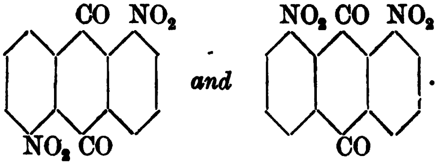


One hundred kilos. of anthraquinone are added to 200–300 kilos. of fuming sulphuric acid (containing 45–50 per cent. of sulphur trioxide) and the mixture is heated at 160–170° until a sample dissolves completely in water and no anthraquinone separates out. (The α-acid is mostly formed at high and the β-acid at low temperatures.) The mixture is heated for an hour longer, the product poured into water, neutralised with sodium hydroxide, and the solution evaporated until the sodium salt of the 2 : 6-acid crystallises out. If this is accompanied by some of the 2-sulphonic acid, they can be separated by taking advantage of their different solubilities in water; the 2-sulphonic acid separates best from slightly acid solutions (Crossley, *J. Amer. Chem. Soc.*, 1915, **37**, 2178). The mother liquor, on evaporation to dryness, furnishes the sodium salt of the 2 : 7-acid.

The α-acid forms small yellow crystals and the β-acid yellow plates; both are readily soluble in water or alcohol, but insoluble in benzene. The sodium salt of the α-acid crystallises with $7H_2O$ and that of the β-acid with $4H_2O$.

The α-acid is used for making Alizarin YCA (various other marks; flavopurpurin) and the β-acid for Alizarin SC (various other marks; anthrapurpurin).

1 : 5- *and* 1 : 8-DINITROANTHRAQUINONES,



Ten parts of anthraquinone are dissolved in 200 parts of sulphuric acid, 10 parts of dry sodium nitrate are stirred in, and the mixture is kept at 60–80° for twelve hours. It is then poured into water and the mixture of 1 : 5- and 1 : 8-dinitroanthraquinones is collected and washed.

Alternatively, 10 parts of anthraquinone are dissolved in 55 parts of sulphuric acid and 10 parts of nitric acid (D 1·48) are added gradually, the temperature being kept below 40°. After two days the mixture is poured into water and the solid collected and dried.

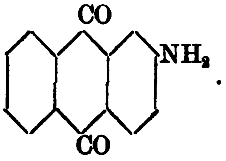
The mixture is generally used without separation, but by repeated extraction with alcohol or acetone the 1 : 5-compound, which constitutes 88 per cent. of the mixture, is left as an insoluble powder (Römer, *Ber.*, 1883, **16**, 366 ; Badische Anilin- & Soda-Fabrik, G.P., 72685).

Böttger and Petersen dissolved anthraquinone in 16 parts of a mixture of equal parts of sulphuric and nitric (D 1·50) acids and heated the solution to boiling for some time (*Annalen*, 1871, **160**, 147).

The 1 : 5-compound melts above 330° and the 1 : 8-compound at 312°.

The mixture, or the 1 : 5-compound, is used for making the various Anthracene blues.

2-AMINOANTHRAQUINONE,



(1) 4·12 Kilos. of sodium anthraquinone-2-sulphonate are dissolved in a solution of 2·36 kilos. of crystallised barium chloride in 3·1 times the quantity of water, 20·5 litres of ammonia (25 per cent.) are added, and the mixture is heated for forty-eight hours at 170–177°, the pressure being 21–22 atmospheres. After cooling, the product is filtered off, and washed successively with water, dilute hydrochloric acid, and dilute sodium hydroxide. The 2-aminoanthraquinone, after being crystallised from chlorobenzene, amounts to 2·19 kilos., or 73·7 per cent. of the theoretical yield. Without the use of barium chloride the yield is only 50 per cent. of the theoretical (Farbwerke vorm. Meister, Lucius, & Brüning, F.P., 469741 ; G.P., 267212 ; U.S.P., 1104943).

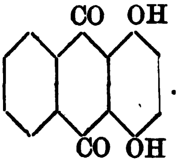
(2) Two hundred and fifty parts of sodium anthraquinone-2-sulphonate (in the form of a 50 per cent. paste) are mixed with 156 parts of manganese dioxide (80 per cent.) and 130 parts of water. Five hundred and eighty parts of ammonia (25 per cent.) are added and the mixture is heated for twenty-four hours at

200°. The 2-aminoanthraquinone can be separated from manganese dioxide by treatment with sulphurous acid or sodium hydrogen sulphite, and is then dried. An almost theoretical yield is obtained. Alternatively, a mixture of 250 parts of sodium anthraquinone-2-sulphonate, 150 parts of sodium dichromate, 50 parts of ammonium chloride, and 600 parts of ammonia (15 per cent.) is heated for twenty to twenty-four hours at 200°. The product, after being freed from chromium oxide, is pure (Badische Anilin- & Soda-Fabrik, E.P., 21710 of 1911; F.P., 444175; G.P., 256515; U.S.P., 1063173). Instead of the above oxidising agents, an aromatic nitro-compound may be employed (Society of Chemical Industry in Basle, E.P., 115259 [1917]; U.S.P., 1255719).

2-Aminoanthraquinone is also obtained (together with the 1-amino-compound) by condensing *m*-aminobenzoylbenzoic acid by means of sulphuric acid (Basle Chemical Works, G.P., 148110), by similar treatment of the carbamide derivative of the same acid (Aktiengesellschaft für Anilinfabrikation, E.P., 8917 of 1914; F.P., 470562), by the hydrolysis of 2-*p*-toluenesulphonylaminoanthraquinone, produced by the action of *p*-toluenesulphonamide on 2-iodoanthraquinone in the presence of copper (Ullmann, E.P. 16272 of 1910; F.P., 418178; G.P., 224982), by the action of ammonia in the presence of oxidising agents on *meso*halogenanthracene-2-sulphonic acids (Badische Anilin- & Soda-Fabrik, G.P., 288996), or by heating 2-chloroanthraquinone with ammonia (Farbenfabriken vorm. F. Bayer & Co., G.P., 295624).

2-Aminoanthraquinone forms red needles melting at 302°. It is used for making Indanthrene (Caledon blue, Chloranthrene blue BD, Duranthrene blue), Indanthrene yellow (Caledon yellow, Chloranthrene yellow), and Indanthrene brown (Caledon brown).

QUINIZARIN,
(1 : 4-DIHYDROXYANTHRAQUINONE)



This compound was obtained by Grimm (*Ber.*, 1873, **6**, 508) by condensing phthalic anhydride with quinol, but only a fraction of the theoretical yield is produced. The following processes have been patented.

(1) *From Anthraquinone*.—(*a*) A mixture of 10 parts of anthra-

quinone, 10 parts of crystallised boric acid, and 200 parts of sulphuric acid is heated. An energetic action sets in at 260–280°, sulphur dioxide is evolved, and the formation of quinizarin is complete in a short time. If the heating is continued, purpurin is formed. The complete formation of quinizarin is ascertained by spectroscopic tests on a sample diluted with sulphuric acid. The mixture is poured into water and the quinizarin filtered off. If necessary, it can be purified by dissolving it in alkali and precipitating with acid. Hydroxyanthraquinonesulphonic acids, which may be formed, can be salted out of the filtrate from the quinizarin (Farbenfabriken vorm. F. Bayer & Co., E.P., 973 of 1894; F.P., 235896; G.P., 81960).

(*b*) Fourteen parts of sodium nitrite are added to 200 parts of cooled sulphuric acid and when all is dissolved 10 parts of anthraquinone and 10 parts of crystallised boric acid are added. The mixture is stirred and heated as quickly as possible to 220–230°. At 180–190°, the reaction takes place, which is complete after heating for two to four hours at 220–230°. When cool, the mixture is poured into water, the whole boiled to decompose the boric ester which is first formed, and the quinizarin is filtered off. Alternatively, gaseous nitrous acid can be passed into a solution of 10 parts of anthraquinone and 10 parts of boric acid in 200 parts of sulphuric acid and the whole heated to 220–230° until the solution is deep red (Farbenfabriken vorm. F. Bayer & Co., E.P., 975 of 1894; addition to F.P., 224740; G.P., 81245).

(*c*) Ten kilos. of sodium nitrite are slowly added to 120 kilos. of sulphuric acid, followed by 7 kilos. of anthraquinone and 1·6 kilos. of mercuric sulphate, and the mixture is heated until, at 180°, the mass is brownish-red. The temperature must not be allowed to rise above this point. When cool, the mass is poured into water, the precipitate dissolved in sodium hydroxide solution and boiled for half an hour, when the solution is filtered from any unchanged anthraquinone and then acidified to obtain the quinizarin (Badische Anilin- & Soda-Fabrik, E.P., 7394 of 1903; F.P., 338529; G.P., 153129; U.S.P., 754264; Farbenfabriken vorm. F. Bayer & Co., E.P., 27373 of 1904; F.P., 348936; G.P., 161954).

(2) *From Erythrohydroxyanthraquinone* (1-*Hydroxyanthraquinone*).—Twenty kilos. of sodium nitrite are dissolved in 600 kilos. of sulphuric acid, and 30 kilos. of boric acid and then 30 kilos. of erythrohydroxyanthraquinone are added. The mixture is heated to 180–200° until a spectroscopic test shows no increase in the amount of quinizarin. The mass is cooled, diluted

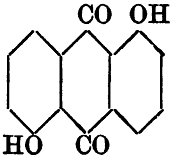
with water, boiled, and the quinizarin filtered off (Farbenfabriken vorm. F. Bayer & Co., E.P., 1499 of 1905 ; F.P., 350957 ; G.P., 162792).

(3) *From Phthalic Anhydride and* p-*Chlorophenol.*—Eighty parts of phthalic anhydride, 20 parts of boric acid, and 23 parts of *p*-chlorophenol are mixed with 400 parts of sulphuric acid and the mixture is heated for three hours at 150°. The temperature is then raised to 180–200° and kept at this point until the amount of quinizarin no longer increases. On cooling, the mass is poured into twenty times its quantity of water and the quinizarin filtered off. It is purified by extraction with a large quantity of boiling water, and dried. The yield is 70–80 per cent. of the theoretical. Alternatively, a solution of 60 parts of *p*-chlorophenol in 200 parts of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide) is heated to 130–140° until a sample, when added to a 12 per cent. solution of salt, gives no precipitate, showing the formation of *p*-chlorophenoldisulphonic acid. Two hundred parts of sulphuric acid, 40 parts of boric acid, and 80 parts of phthalic anhydride are now added and the mixture is heated as described above. After some time, dark blue crystals of the ester, $C_{14}H_8O_4,SO_3,B_2O_3$, separate out. When the quantity of this no longer increases, the mass is cooled, and the ester filtered on an asbestos filter, washed with sulphuric acid (60° Bé.), and finally with ice-water. On boiling it with water or sodium carbonate solution it is converted into quinizarin (Farbenfabriken vorm. F. Bayer & Co., E.P., 12619 of 1912 ; F.P., 452244 ; G.P., 255031 ; U.S.P., 1087412).

Quinizarin forms red plates or needles which melt at 195° and dissolve in alkalis with a blue colour.

It is used for making Alizarin cyanine green (Kymric green) and Alizarin irisol.

ANTHRARUFIN,
(1 : 5-DIHYDROXYANTHRAQUINONE)



(1) Ten kilos. of 1-hydroxyanthraquinone are dissolved in 200 kilos. of fuming sulphuric acid (containing 80 per cent. of sulphur trioxide) and the solution is allowed to remain at a temperature not exceeding 30° until a sample, when worked up as described below and dissolved in sulphuric acid, gives a solution like one of pure anthrarufin. The sulphuric ether of anthrarufin

which is obtained on pouring the mixture into water is converted into anthrarufin by heating it with acids or dissolving it in alkali and decomposing with acid (Farbenfabriken vorm. F. Bayer & Co., G.P., 97674).

(2) Fifty kilos. of anthraquinone and 20 kilos. of boric acid (dried at 100°) are dissolved in 1,000 kilos. of fuming sulphuric acid (containing 80 per cent. of sulphur trioxide). The pan is closed and the mixture heated for thirty-six hours at 100°, the pressure being 5–7 atmospheres. After cooling, 1,000 kilos. of sulphuric acid (60° Bé.) are added and the whole is poured into water. The precipitate, which contains the sulphuric ether of anthrarufin, is collected, washed, dissolved in dilute sodium hydroxide, and the solution filtered from any unchanged anthraquinone. The boiling filtrate is treated with sulphuric or hydrochloric acid and the precipitated anthrarufin is filtered off. It can be obtained free from a small amount of quinizarin by treatment with solvents or by fractional precipitation of its alkali solution (Farbenfabriken vorm. F. Bayer & Co., G.P., 101220).

(3) Ten kilos. of 1 : 5-dinitroanthraquinone are heated with 50 kilos. of pyridine in an autoclave for four hours at 180–200°. The pyridine is removed by distillation or by means of a current of steam. The anthrarufin is extracted from the residue by boiling with very dilute sodium hydroxide solution and acidifying the filtered solution (Farbenfabriken vorm. F. Bayer & Co., G.P., 145238).

The dinitroanthraquinone (10 kilos.) may also be heated with 10 kilos. of quicklime and 200 litres of water in an autoclave fitted with a stirrer for twelve to fifteen hours at 190–200°. The product is treated with boiling dilute hydrochloric acid, the mass filtered, and the anthrarufin extracted from the residue by means of dilute sodium hydroxide solution (*idem*, G.P., 158891).

If the crude mixture of 1 : 5- and 1 : 8-dinitroanthraquinones is reduced, the diamino-compounds diazotised and boiled with acid, a mixture of anthrarufin and chrysazin is obtained which can be separated by means of hot benzene (Farbwerke vorm. Meister, Lucius, & Brüning, G.P., 97688).

(4) Ten kilos. of dry sodium anthraquinone-α-sulphonate are added to 30 kilos. of fuming sulphuric acid (containing 25–30 per cent. of sulphur trioxide) and the solution is heated for five to six hours at 150°. The solution is poured into water and the sodium salt of 1-hydroxyanthraquinone-5-sulphonic acid isolated in the

usual way. On heating it with milk of lime under pressure, it is converted into anthrarufin (*idem*, G.P., 158413).

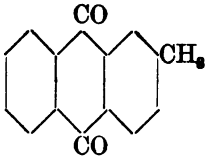
(5) Twenty-five kilos. of sodium anthraquinone-1 : 5-disulphonate are heated with 30 kilos. of quicklime and 400 litres of water in an autoclave fitted with a stirrer for twelve hours at 180–190°. Alternatively, 50 kilos. of potassium anthraquinone 1 : 5-disulphonate are heated with 30 kilos. of quicklime, 50 kilos. of sodium hydroxide solution (27 per cent.), and 750 litres of water for ten hours under a pressure of 12 atmospheres (compare Schmidt, *Ber.*, 1904, **37**, 69). The product is worked up as described under (3) (Farbenfabriken vorm. F. Bayer & Co., E.P., 25541 of 1903; G.P., 170108; Iljinsky and Wedekind & Co., E.P., 10242 of 1903; F.P., 333144; G.P., 149801, 157123, 170108; U.S.P., 742910, 743664).

Modifications of this process consist in heating a mixture of 100 parts of a 44 per cent. paste of potassium anthraquinone-1 : 5-disulphonate, 90 parts of sodium hydroxide solution (27 per cent.), 50 parts of barium chloride and 600 parts of water for twelve hours under a pressure of 10 atmospheres (Farbenfabriken vorm. F. Bayer & Co., E.P., 1062 of 1905; addition of Jan. 17th, 1905, to F.P., 336867; G.P., 172642), or a mixture of 100 parts of calcium anthraquinone-1 : 5-disulphonate, 500 parts of hot water in which 100 parts of quicklime are slaked, 30 parts of potassium nitrate and 100 parts of calcium chloride solution (20 per cent.) in an autoclave at 180–200° until no more hydroxy-sulphonic acid (the intermediate substance) is present. On precipitation with hydrochloric acid, about 50 parts of pure anthrarufin are obtained (Iljinsky and Wedekind & Co., E.P., 25738 of 1903; F.P., 336938; G.P., 195874; U.S.P., 778670).

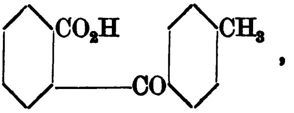
Anthrarufin forms yellow tablets which melt at 280° and are almost insoluble in water, sparingly soluble in alcohol, ether, carbon disulphide, or glacial acetic acid, but more readily so in benzene. Its solution in alkali hydroxides is yellow.

It is used for making Alizarin saphirol B and SE (Solway blue).

2-METHYLANTHRAQUINONE,



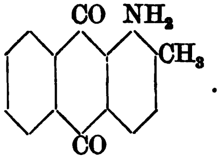
Fifty grams of phthalic anhydride and 200 grams of toluene are mixed together and 100 grams of powdered aluminium chloride are added. Hydrogen chloride is evolved and the mixture becomes warm. After ten hours, water is added, excess of toluene is distilled off in a current of steam, and the aqueous solution poured off; a little phthalic acid may be recovered from it on acidifying. The remaining cake is rendered alkaline with sodium carbonate, steam passed in for four to five hours, the whole filtered, and the filtrate acidified, whereby 2-*p*-toluoylbenzoic acid (m. p. 146°),



is precipitated (79 grams) in a yield of 97 per cent. of the theoretical. The acid is now dissolved in 9 parts of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide) and heated on the water-bath for 1½ hours. On pouring into water, 2-methylanthraquinone is obtained and is filtered off and dried (Heller and Schülke, *Ber.*, 1908, **41**, 3632; compare Elbs, *J. pr. Chem.*, 1886, [ii], **33**, 318; Limpricht and Wiegand, *Annalen*, 1900, **311**, 178).

2-Methylanthraquinone crystallises in pale yellow needles melting at 177°, and is soluble in acetic acid or benzene, but sparingly so in ether. It is used for making Anthraflavone G, Cibanone orange R, and Cyananthrol R and G.

1-AMINO-2-METHYLANTHRAQUINONE,



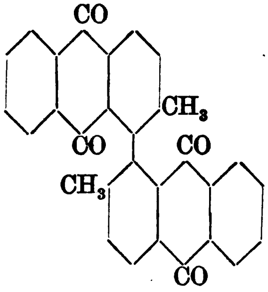
Two parts of methylanthraquinone are dissolved in six to seven times the quantity of sulphuric acid, and 1 part of potassium nitrate (or the equivalent amount of sodium nitrate) is added gradually, the whole being cooled. A greenish-yellow, crystalline mass is obtained which, after twenty-four hours, is poured into water, and the yellow product is filtered off, washed, and boiled with alcohol until the extract is pale yellow. 1-Nitro-2-methylanthraquinone, when crystallised from glacial acetic acid, melts at 269–270°; it is very sparingly soluble in alcohol, ether, benzene, chloroform, or acetic acid, but readily so in xylene, nitrobenzene, or aniline (Römer and Link, *Ber.*, 1883, **16**, 695).

For the reduction, 1 part of the nitro-compound is treated with 5 parts of crystallised sodium sulphide and 600–800 parts of water (Badische Anilin- & Soda-Fabrik, E.P., 20718 of 1900; F.P., 307912; G.P., 131873; U.S.P., 715662) or 1 part of the nitro-compound is boiled with 3½ parts of crystallised sodium sulphide and 20 parts of water for an hour (Römer and Link used stannous hydroxide), and, if necessary, the amino-compound is crystallised from glacial acetic acid (Scholl and Holdermann, *Ber.*, 1907, **40**, 1696).

1-Amino-2-methylanthraquinone melts at 202° and is insoluble in water, but readily soluble in alcohol, ether, benzene, or acetic acid.

It is used for making 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl.

2 : 2′-DIMETHYL-1 : 1′-DIANTHRAQUINONYL,



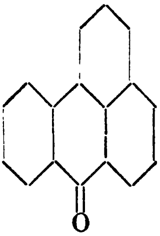
Twenty parts of 1-amino-2-methylanthraquinone are dissolved in 250 parts of sulphuric acid (97 per cent.), and 8 parts of solid sodium nitrite are added gradually at the ordinary temperature. When the diazotisation is complete, the product is poured on 500 parts of ice, and after three hours the diazonium sulphate is filtered off, washed successively with a little cold water, alcohol, and ether, and dried in the air. Ten parts are then stirred with 60–80 parts of acetic anhydride, and 2 parts of copper powder (" copper bronze ") are added. Nitrogen is evolved and a violet solution is obtained from which, after a few hours, a yellowish-white precipitate separates out. This is warmed on the water-bath, filtered, and the residue suspended in hot water to destroy acetic anhydride, then treated with dilute nitric acid to dissolve copper, and filtered off.

The compound can also be prepared by heating 1-iodo-, 1-chloro-, or 1-bromo-methylanthraquinone (prepared from the 1-amino-compound by the diazo-reaction) with copper powder (Badische Anilin- & Soda-Fabrik, E.P., 14578 of 1905; F.P., 357239; G.P., 180157; U.S.P., 856811; Scholl and Kunz, *Ber.*, 1907, **40**, 1697).

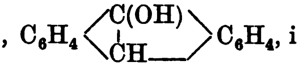
2 : 2′-Dimethyl-1 : 1′-dianthraquinonyl melts at 366–367° and is readily soluble in boiling aniline or nitrobenzene, but sparingly so in boiling xylene. The sulphuric acid solution is yellow.

It is used for making Indanthrene gold orange G.

Benzanthrone,



This is prepared by condensing glycerol and anthranol by means of sulphuric acid.

Preparation of Anthranol.—Ten grams of anthraquinone are boiled with 400–500 grams of glacial acetic acid and 25 grams of granulated tin added. About 10 c.c. of fuming hydrochloric acid are poured in and the yellow colour changes to brown, which, however, soon disappears. Small quantities of hydrochloric acid are added to the boiling liquid as long as the colour changes to brown and in order to maintain a constant production of hydrogen. The process is finished after fifteen minutes, the end of the reaction being shown by a sample, on cooling, remaining clear and giving no precipitate of anthraquinone. The whole is then poured into water and acidified with hydrochloric acid, when anthranol,  $C_6H_4\left\langle\begin{matrix}C(OH)\\|\\CH\end{matrix}\right\rangle C_6H_4$, is obtained in a yield of more than 80 per cent. of the theoretical. It melts and decomposes at 163–170° and can be obtained pure by crystallisation from glacial acetic acid (Liebermann and Gimbel, *Ber.*, 1887, **20**, 1854).

The reduction can also be effected as follows: Fifty parts of finely powdered anthraquinone are heated to 200° or higher in an iron autoclave fitted with a stirrer, with 10 parts of iron and 1,000 parts of aqueous ferrous chloride (50 per cent.) until a test portion of the melted product dissolves in sodium hydroxide to a yellow solution. After cooling, the precipitate is filtered off and washed with water. The residue is dissolved in sodium hydroxide solution and strained directly into hydrochloric acid. The precipitated anthranol melts at 152°. If the process is conducted in acetic acid suspension the heating can be performed in an open vessel or in a reflux apparatus (Chemische Fabrik Griesheim-Elektron, E.P., 1728 of 1911; F.P., 426994).

Benzanthrone.—Ten parts of anthranol are dissolved or suspended in 150 parts of sulphuric acid (62° Bé.) and 10 parts of glycerol are added. The mixture is carefully warmed; at 120°, it begins to turn red and sulphur dioxide is evolved. When the reaction is complete (after 4 hours at 120°) the cooled mass is poured into water, and the product separates in olive-green flocks, which are collected, washed, boiled for half an hour with 13 times the quantity of sodium hydroxide solution (1 per cent.), pressed, and dried. The crude substance is an olive-green powder insoluble in dilute acids or alkalis, but dissolves in sulphuric acid with a reddish-brown colour and deep orange fluorescence. It crystallises from alcohol in pale yellow needles melting at 170° (Badische Anilin- & Soda-Fabrik, E.P., 16538 of 1904; F.P., 349531; G.P., 171939, 176018; U.S.P., 787859).

The preparation of anthranol may be combined with that of benzanthrone as follows: 1 part of anthraquinone is stirred into 40 parts of sulphuric acid (82 per cent.), 2 parts of aniline sulphate are added, the mass is warmed slowly to 100°, and then treated with a mixture of 1 part of glycerol with 3 parts of sulphuric acid (82 per cent.). The temperature rises spontaneously to 120° and the further treatment is as described above (Bally and Scholl, *Ber.*, 1911, **44**, 1666).

It can be prepared directly from anthracene as follows:—

Fifty kilos. of anthracene (98 per cent.) are dissolved in 1,500 kilos. of sulphuric acid (62° Bé.), 100 kilos. of glycerol are added, and the whole is slowly heated to 100–110° and kept at this point until the anthracene has disappeared. The brownish-red mass is poured into water, sodium chloride added, and the mixture filtered. The dry product contains a substance soluble in water and benzanthrone, which is insoluble (Badische Anilin- & Soda-Fabrik, E.P., 16538 of 1904; F.P., 349531; G.P., 176019; U.S.P., 787859).

Benzanthrone is also obtained by condensing 2-aminoanthraquinone with dichlorohydrin, or anthranol with acetin (*idem*, G.P., 204354).

Another process consists in heating a mixture of phenyl α-naphthyl ketone and 10 parts of aluminium chloride for 2½ hours gradually up to 150°. On cooling, the red mass is treated slowly with water and the residue washed with dilute hydrochloric acid, alcohol, and ether, when benzanthrone remains.

Alternatively, a mixture of 5 parts of the ketone and 30 parts of anhydrous ferric chloride is heated within half an hour to 70–100° and then for one to two hours at 100–120° (Badische Anilin- & Soda-Fabrik, E.P., 16271 of 1910 ; F.P., 418435 ; G.P., 239761).

The synthesis of benzanthrone from 3 : 4-benzofluorenone has recently been described (Schaarschmidt, *Ber.*, 1917, **50**, 294 ; 1918, **51**, 1074, 1082).

Benzanthrone melts at 170° and is used for making Indanthrene dark blue BO (Caledon purple), Indanthrene green B (Caledon green) and Indanthrene violet R extra (Caledon violet).

APPENDIX

SULPHURIC ACID.

Specific gravity of pure sulphuric acid at 15° compared with water at 4° (Lunge, "Technical Chemists' Handbook").

Spec. gravity	Per cent. H_2SO_4	Spec. gravity.	Per cent. H_2SO_4	Spec. gravity.	Per cent. H_2SO_4	Spec. gravity.	Per cent. H_2SO_4
1·200	27·32	1·395	49·59	1·590	67·83	1·780	84·50
1·205	27·95	1·400	50·11	1·595	68·26	1·785	85·10
1·210	28·58	1·405	50·63	1·600	68·70	1·790	85·70
1·215	29·21	1·410	51·15	1·605	69·13	1·795	86·30
1·220	29·84	1·415	51·66	1·610	69·56	1·800	86·92
1·225	30·48	1·420	52·15	1·615	70·00	1·805	87·60
1·230	31·11	1·425	52·63	1·620	70·42	1·810	88·30
1·235	31·70	1·430	53·11	1·625	70·85	1·815	89·05
1·240	32·28	1·435	53·59	1·630	71·27	1·820	90·05
1·245	32·86	1·440	54·07	1·635	71·70	1·821	90·20
1·250	33·43	1·445	54·55	1·640	72·12	1·822	90·40
1·255	34·00	1·450	55·03	1·645	72·55	1·823	90·60
1·260	34·57	1·455	55·50	1·650	72·96	1·824	90·80
1·265	35·14	1·460	55·97	1·655	73·40	1·825	91·00
1·270	35·71	1·465	56·43	1·660	73·81	1·826	91·25
1·275	36·29	1·470	56·90	1·665	74·24	1·827	91·50
1·280	36·87	1·475	57·37	1·670	74·66	1·828	91·70
1·285	37·45	1·480	57·83	1·675	75·08	1·829	91·90
1·290	38·03	1·485	58·28	1·680	75·50	1·830	92·10
1·295	38·61	1·490	58·74	1·685	75·86	1·831	92·43
1·300	39·19	1·495	59·22	1·690	76·30	1·832	92·70
1·305	39·77	1·500	59·70	1·695	76·73	1·833	92·97
1·310	40·35	1·505	60·18	1·700	77·17	1·834	93·25
1·315	40·93	1·510	60·65	1·705	77·60	1·835	93·56
1·320	41·50	1·515	61·12	1·710	78·04	1·836	93·80
1·325	42·08	1·520	61·59	1·715	78·48	1·837	94·20
1·330	42·66	1·525	62·06	1·720	78·92	1·838	94·60
1·335	43·20	1·530	62·53	1·725	79·36	1·839	95·00
1·340	43·74	1·535	63·00	1·730	79·80	1·840	95·60
1·345	44·28	1·540	63·43	1·735	80·24	1·8405	95·95
1·350	44·82	1·545	63·85	1·740	80·68	1·8410	96·30
1·355	45·35	1·550	64·26	1·745	81·12	1·8415	97·35
1·360	45·88	1·555	64·67	1·750	81·56	1·8410	98·20
1·365	46·41	1·560	65·20	1·755	82·00	1·8405	98·52
1·370	46·94	1·565	65·65	1·760	82·44	1·8400	98·72
1·375	47·47	1·570	66·09	1·765	83·01	1·8395	98·77
1·380	48·00	1·575	66·53	1·770	83·41	1·8390	99·12
1·385	48·53	1·580	66·95	1·775	84·02	1·8385	99·31
1·390	49·06	1·585	67·40				

NITRIC ACID.

Specific gravity of nitric acid at 15° compared with water at 4° and reduced to vacuum (Lunge and Rey).

Spec. gravity	Per cent. HNO_3 by weight.	Spec. gravity.	Per cent. HNO_3 by weight.	Spec. gravity.	Per cent. HNO_3 by weight.	Spec. gravity.	Per cent. HNO_3 by weight.
1·000	0·10	1·155	25·60	1·310	49·07	1·460	79·98
1·005	1·00	1·160	26·36	1·315	49·89	1·465	81·42
1·010	1·90	1·165	27·12	1·320	50·71	1·470	82·90
1·015	2·80	1·170	27·88	1·325	51·53	1·475	84·45
1·020	3·70	1·175	28·63	1·330	52·37	1·480	86·05
1·025	4·60	1·180	29·38	1·335	53·22	1·485	87·70
1·030	5·50	1·185	30·13	1·340	54·07	1·490	89·60
1·035	6·38	1·190	30·88	1·345	54·93	1·495	91·60
1·040	7·26	1·195	31·62	1·350	55·79	1·500	94·09
1·045	8·13	1·200	32·36	1·355	56·66	1·501	94·60
1·050	8·99	1·205	33·09	1·360	57·57	1·502	95·08
1·055	9·84	1·210	33·82	1·365	58·48	1·503	95·55
1·060	10·68	1·215	34·55	1·370	59·39	1·504	96·00
1·065	11·51	1·220	35·28	1·375	60·30	1·505	96·39
1·070	12·33	1·225	36·03	1·380	61·27	1·506	96·76
1·075	13·15	1·230	36·78	1·385	62·24	1·507	97·13
1·080	13·95	1·235	37·53	1·390	63·23	1·508	97·50
1·085	14·74	1·240	38·29	1·395	64·25	1·509	97·84
1·090	15·53	1·245	39·05	1·400	65·30	1·510	98·10
1·095	16·32	1·250	39·82	1·405	66·40	1·511	98·32
1·100	17·11	1·255	40·58	1·410	67·50	1·512	98·53
1·105	17·89	1·260	41·34	1·415	68·63	1·513	98·73
1·110	18·67	1·265	42·10	1·420	69·80	1·514	98·90
1·115	19·45	1·270	42·87	1·425	70·98	1·515	99·07
1·120	20·23	1·275	43·64	1·430	72·17	1·516	99·21
1·125	21·00	1·280	44·41	1·435	73·39	1·517	99·34
1·130	21·77	1·285	45·18	1·440	74·68	1·518	99·46
1·135	22·54	1·290	45·95	1·445	75·98	1·519	99·57
1·140	23·31	1·295	46·72	1·450	77·28	1·520	99·67
1·145	24·08	1·300	47·49	1·455	78·60	1·530	100·0
1·150	24·84	1·305	48·26				

For corrections for temperature and the presence of oxides of nitrogen, see Lunge, "Sulphuric Acid and Alkali," 4th ed., vol. I, pp. 136, 137.

HYDROCHLORIC ACID.

Specific gravity of pure hydrochloric acid at 15° compared with water at 4° and reduced to vacuum (Lunge and Marchlewski).

Spec. gravity	Per cent. HCl.	Spec. gravity.	Per cent. HCl.	Spec. gravity.	Per cent. HCl.	Spec. gravity.	Per cent. HCl.
1·000	0·016	1·055	11·18	1·105	20·97	1·155	30·55
1·005	0·15	1·060	12·19	1·110	21·92	1·160	31·52
1·010	2·14	1·065	13·19	1·115	22·86	1·165	32·49
1·015	3·12	1·070	14·17	1·120	23·82	1·170	33·46
1·020	4·13	1·075	15·16	1·125	24·78	1·175	34·42
1·025	5·15	1·080	16·15	1·130	25·75	1·180	35·39
1·030	6·15	1·085	17·13	1·135	26·70	1·185	36·31
1·035	7·15	1·090	18·11	1·140	27·66	1·190	37·23
1·040	8·16	1·095	19·06	1·145	28·61	1·195	38·16
1·045	9·16	1·100	20·01	1·150	29·57	1·200	39·11
1·050	10·17						

To reduce the specific gravity of HCl solution observed at t^1° C. to t^2° C. add $0{\cdot}00047 \times (t^1 - t^2)$.

SODIUM HYDROXIDE.

Specific gravity of sodium hydroxide solutions at 15° (Lunge)

Spec. gravity	Per cent. NaOH	Spec. gravity.	Per cent. NaOH	Spec. gravity.	Per cent. NaOH	Spec. gravity.	Per cent. NaOH
1·005	0·43	1·140	12·49	1·275	24·58	1·405	37·17
1·010	0·86	1·145	12·94	1·280	25·04	1·410	37·65
1·015	1·28	1·150	13·34	1·285	25·50	1·415	38·16
1·020	1·69	1·155	13·76	1·290	25·96	1·420	38·67
1·025	2·13	1·160	14·19	1·295	26·41	1·425	39·17
1·030	2·60	1·165	14·62	1·300	26·85	1·430	39·67
1·035	3·06	1·170	15·06	1·305	27·35	1·435	40·18
1·040	3·50	1·175	15·53	1·310	27·85	1·440	40·68
1·045	3·90	1·180	16·00	1·315	28·34	1·445	41·20
1·050	4·34	1·185	16·45	1·320	28·83	1·450	41·70
1·055	4·76	1·190	16·91	1·325	29·32	1·455	42·22
1·060	5·20	1·195	17·36	1·330	29·80	1·460	42·75
1·065	5·67	1·200	17·81	1·335	30·28	1·465	43·27
1·070	6·13	1·205	18·26	1·340	30·74	1·470	43·80
1·075	6·58	1·210	18·71	1·345	31·20	1·475	44·33
1·080	7·05	1·215	19·18	1·350	31·75	1·480	44·85
1·085	7·50	1·220	19·65	1·355	32·28	1·485	45·37
1·090	7·95	1·225	20·12	1·360	32·79	1·490	45·89
1·095	8·39	1·230	20·60	1·365	33·26	1·495	46·42
1·100	8·78	1·235	21·03	1·370	33·73	1·500	46·94
1·105	9·23	1·240	21·47	1·375	34·22	1·505	47·47
1·110	9·67	1·245	21·90	1·380	34·71	1·510	48·00
1·115	10·12	1·250	22·33	1·385	35·20	1·515	48·53
1·120	10·56	1·255	22·77	1·390	35·68	1·520	49·05
1·125	11·06	1·260	23·23	1·395	36·15	1·525	49·58
1·130	11·55	1·265	23·68	1·400	36·67	1·530	50·10
1·135	12·02	1·270	24·13				

Comparison of the hydrometer degrees according to Baumé and Twaddell, with the specific gravities.

Bé.	Tw.	Spec. gravity.	Bé.	Tw.	Spec. gravity.	Bé.	Tw.	Spec. gravity.
0	0	1·000	15·4	24·0	1·120	29·3	51·0	1·255
0·7	1·0	1·005	16·0	25·0	1·125	29·7	52·0	1·260
1·0	1·4	1·007	16·5	26·0	1·130	30·0	52·6	1·263
1·4	2·0	1·010	17·0	26·8	1·134	30·2	53·0	1·265
2·0	2·8	1·014	17·1	27·0	1·135	30·6	54·0	1·270
2·1	3·0	1·015	17·7	28·0	1·140	31·0	54·8	1·274
2·7	4·0	1·020	18·0	28·4	1·142	31·1	55·0	1·275
3·0	4·4	1·022	18·3	29·0	1·145	31·5	56·0	1·280
3·4	5·0	1·025	18·8	30·0	1·150	32·0	57·0	1·285
4·0	5·8	1·029	19·0	30·4	1·152	32·4	58·0	1·290
4·1	6·0	1·030	19·3	31·0	1·155	32·8	59·0	1·295
4·7	7·0	1·035	19·8	32·0	1·160	33·0	59·4	1·297
5·0	7·4	1·037	20·0	32·4	1·162	33·3	60·0	1·300
5·4	8·0	1·040	20·3	33·0	1·165	33·7	61·0	1·305
6·0	9·0	1·045	20·9	34·0	1·170	34·0	61·6	1·308
6·7	10·0	1·050	21·0	34·2	1·171	34·2	62·0	1·310
7·0	10·2	1·052	21·4	35·0	1·175	34·6	63·0	1·315
7·4	11·0	1·055	22·0	36·0	1·180	35·0	64·0	1·320
8·0	12·0	1·060	22·5	37·0	1·185	35·4	65·0	1·325
8·7	13·0	1·065	23·0	38·0	1·190	35·8	66·0	1·330
9·0	13·4	1·067	23·5	39·0	1·195	36·0	66·4	1·332
9·4	14·0	1·070	24·0	40·0	1·200	36·2	67·0	1·335
10·0	15·0	1·075	24·5	41·0	1·205	36·6	68·0	1·340
10·6	16·0	1·080	25·0	42·0	1·210	37·0	69·0	1·345
11·0	16·6	1·083	25·5	43·0	1·215	37·4	70·0	1·350
11·2	17·0	1·085	26·0	44·0	1·220	38·7	71·0	1·355
11·9	18·0	1·090	26·4	45·0	1·225	38·0	71·4	1·357
12·0	18·2	1·091	26·9	46·0	1·230	38·2	72·0	1·360
12·4	19·0	1·095	27·0	46·2	1·231	38·6	73·0	1·365
13·0	20·0	1·100	27·4	47·0	1·235	39·0	74·0	1·370
13·6	21·0	1·105	27·9	48·0	1·240	39·4	75·0	1·375
14·0	21·6	1·108	28·0	48·2	1·241	39·8	76·0	1·380
14·2	22·0	1·110	28·4	49·0	1·245	40·0	76·6	1·383
14·9	23·0	1·115	28·8	50·0	1·250	40·1	77·0	1·385
15·0	23·2	1·116	29·0	50·4	1·252	40·5	78·0	1·390

N.B.—The Baumé degrees are calculated by the formula $d=\frac{144{\cdot}3}{144{\cdot}3-n}$, water at 15° C. being put = 0° and sulphuric acid of 1·842 at 15° C. = 66° A different scale for Baumé's hydrometer is used in America.

Comparison of the hydrometer degrees according to Baumé and Twaddell, with the specific gravities—(*continued*).

Bé.	Tw.	Spec. gravity.	Bé.	Tw.	Spec. gravity.	Bé.	Tw.	Spec. gravity.
40·8	79·0	1·395	50·9	109·0	1·545	59·5	140·0	1·700
41·0	79·4	1·397	51·0	109·2	1·546	59·7	141·0	1·705
41·2	80·0	1·400	51·2	110·0	1·550	60·0	142·0	1·710
41·6	81·0	1·405	51·5	111·0	1·555	60·2	143·0	1·715
42·0	82·0	1·410	51·8	112·0	1·560	60·4	144·0	1·720
42·3	83·0	1·415	52·0	112·6	1·563	60·6	145·0	1·725
42·7	84·0	1·420	52·1	113·0	1·565	60·9	146·0	1·730
43·0	84·8	1·424	52·4	114·0	1·570	61·0	146·4	1·732
43·1	85·0	1·425	52·7	115·0	1·575	61·1	147·0	1·735
43·4	86·0	1·430	53·0	116·0	1·580	61·4	148·0	1·740
43·8	87·0	1·435	53·3	117·0	1·585	61·6	149·0	1·745
44·0	87·6	1·438	53·6	118·0	1·590	61·8	150·0	1·750
44·1	88·0	1·440	53·9	119·0	1·595	62·0	150·6	1·753
44·4	89·0	1·445	54·0	119·4	1·597	62·1	151·0	1·755
44·8	90·0	1·450	54·1	120·0	1·600	62·3	152·0	1·760
45·0	90·6	1·453	54·4	121·0	1·605	62·5	153·0	1·765
45·1	91·0	1·455	54·7	122·0	1·610	62·8	154·0	1·770
45·4	92·0	1·460	55·0	123·0	1·615	63·0	155·0	1·775
45·8	93·0	1·465	55·2	124·0	1·620	63·2	156·0	1·780
46·0	93·6	1·468	55·5	125·0	1·625	63·5	157·0	1·785
46·1	94·0	1·470	55·8	126·0	1·630	63·7	158·0	1·790
46·4	95·0	1·475	56·0	127·0	1·635	64·0	159·0	1·795
46·8	96·0	1·480	56·3	128·0	1·640	64·2	160·0	1·800
47·0	96·6	1·483	56·6	129·0	1·645	64·4	161·0	1·805
47·1	97·0	1·485	56·9	130·0	1·650	64·6	162·0	1·810
47·4	98·0	1·490	57·0	130·4	1·652	64·8	163·0	1·815
47·8	99·0	1·495	57·1	131·0	1·655	65·0	164·0	1·820
48·0	99·6	1·498	57·4	132·0	1·660	65·2	165·0	1·825
48·1	100·0	1·500	57·7	133·0	1·665	65·5	166·0	1·830
48·4	101·0	1·505	57·9	134·0	1·670	65·7	167·0	1·835
48·7	102·0	1·510	58·0	134·2	1·671	65·9	168·0	1·840
49·0	103·0	1·515	58·2	135·0	1·675	66·0	168·4	1·842
49·4	104·0	1·520	58·4	136·0	1·680	66·1	169·0	1·845
49·7	105·0	1·525	58·7	137·0	1·685	66·3	170·0	1·850
50·0	106·0	1·530	58·9	138·0	1·690	66·5	171·0	1·855
50·3	107·0	1·535	59·0	138·2	1·691	66·7	172·0	1·860
50·6	108·0	1·540	59·2	139·0	1·695	67·0	173·0	1·865

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